Title: SOLID THIOCARBONATES AND METHODS OF MANUFACTURE AND USE

Abstract

Stabilized solid thiocarbonates are produced by a process in which water is evaporated from a stabilized aqueous thiocarbonate solution which contains a stabilizing amount of a sulfide, a polysulfide and/or a base.
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SOLID THIOCARBONATES AND
METHODS OF MANUFACTURE AND USE

RELATED APPLICATIONS

This application is a continuation-in-part of copending applications Serial Nos. 07/262,961 for Stabilized Thiocarbonate Solutions and 07/262,962 for Thiocarbonate Solutions, both filed October 28, 1988.

Field of the Invention

This invention relates to the manufacture of salts of thiocarbonic acids. In one of its more particular aspects this invention relates to a process for producing thiocarbonate salts in solid form.

BACKGROUND OF THE INVENTION

Among the more economically serious plant parasites are nematodes, which are roundworms, comprising as many as 10,000 species, of which at least 150 are known to adversely affect plant life. Plant parasitic nematodes have been known since about the year 1750. Most of the nematodes which cause crop damage do so by feeding on plant roots, and therefore are found primarily in the upper few inches of soil in the roots or in close proximity to the roots. Nematode feeding
causes hypertrophy or gall formation, and the evidence of heavy infestation is plant stunting, pale foliage, wilting, and even plant death in extreme cases.

Virtually all of the world's crops and ornamental plants can be attacked by parasitic nematodes. Important destructive nematode species include the root knot nematodes which are hosted by tomatoes, alfalfa, cotton, corn, potatoes, citrus and many other crops, the golden nematode of potatoes, the sugar beet cyst nematode and the citrus nematode. These, and a few other species, are described in "The Soil Pest Complex", Agricultural and Food Chemistry, Vol. 3, pages 202-205 (1955). Also described therein is a further complication resulting from nematode infestation, namely a lowered resistance to the effects of plant attack by bacteria and pathogenic soil fungi.

Except for small volumes of soil which can be sterilized, it has not been found possible to eliminate nematodes. Parasite populations can, however, be kept at levels which economically permit agricultural operations by soil fumigation, crop rotation using non-hosting plant varieties, and (to a much lesser extent) the development of plants which are resistant to infestation. In many instances, control of nematodes is achieved only by combinations of these techniques, and most control programs have proven quite costly.

Another serious problem in agriculture is the attack of plants by pathogenic microorganisms, particularly fungi. Such pathogens are normally controlled by fumigation, prior to crop planting, using broad spectrum biocides, many of which are no longer regarded as environmentally safe. Certain narrow spectrum fungi-
cides are available, but are extremely expensive and lose effectiveness against successive generations of fungi, due to genetic adaptability.

Carbon disulfide is the first reported soil fumigant, used in Europe during the 1870's to control the sugar beet nematode. This agent is commercially impractical, however, since very large quantities must be applied, due to its high volatility. Further, the material is quite flammable, reportedly being ignited even by static electricity resulting from pouring the material out of drums. In addition, carbon disulfide possesses a very objectionable odor, and its vapors are toxic to humans. When sold for fumigant use, the carbon disulfide is normally mixed with an inert fire retarding compound, such as carbon tetrachloride, and occasionally also with another fumigant. Typically, these compositions do not contain over about 20 percent by weight of carbon disulfide.

In addition to soil uses, carbon disulfide has been proven effective in the fumigation of commodities, as an insecticide, as a rodenticide, and for controlling certain weeds.

Numerous compositions possessing nematocidal properties have been developed, including active ingredients such as the polyamines of U.S. Patent 2,979,434 to Santmyer, the heterocyclic compounds of U.S. Patent 2,086,907 to Hessel, and various halogenated compounds. Among the useful halogen-containing nematocides are 1,2-dibromoethane, methyl bromide, 3-bromopropyne, 1,2-dichloropropane, ethylene dichloride and others, all of which are quite phytotoxic, therefore restricting their utility to mostly preplant treatments.
One compound which enjoyed considerable commercial success is 1,2-dibromo-3-chloropropane (DBCP), which can be used to control nematodes in soils with growing perennial plants. However, use of this material has been limited due to a finding of undesirable reproductive system effects in workers exposed to the chemical, and the possibility that the compound is a carcinogen. The unavailability of DBCP has been a serious setback to growers of perennial crops, such as grapes, stone fruits and nuts, since these crops experience more severe cumulative nematode population increases, and most replacement soil fumigants are phytotoxic. U.S. patents concerned with the use of DBCP as a soil fumigant include 2,937,936 to Schmidt and 3,049,472 to Swezey.

A further class of materials used to control nematodes includes some thiocarbonates. U.S. Patent 2,676,129 to Bashour describes the preparation of lower aliphatic disubstituted trithiocarbonates having the structure as in (1):

\[ S = C \begin{array}{c} \text{SR}_1 \\ \text{SR}_2 \end{array} \]  

(1)

wherein \( R_1 \) and \( R_2 \) are alkyl radicals having from three to nine carbon atoms. The compounds were dissolved in acetone and added to nematode-infested soils, resulting in control of the nematodes.

Other compounds have been reported by Seifter in U.S. Patents 2,836,532 and 2,836,533, the former relating to the use of sodium and potassium trithiocar-
bonate, and the latter pertaining to alkali metal and ammonium salts of tetrathioperoxyctonic acid. Both are described as effective in nematode control.

These references state that "not all carbon disulfide derivatives are effective nematode toxicants." Furthermore, U.S. Patent 2,836,532 points out that sodium trithiocarbonate is unexpectedly superior to potassium trithiocarbonate as a nematocide.

Another serious problem in agriculture is that of low nitrogen use-efficiency, since crops have been found to recover only 30 to 70 percent of the total amount of expensive fertilizer nitrogen which is applied to the soil. Most of the lost nitrogen is due to nitrite and nitrate ions, which are exceptionally mobile in a soil environment, and therefore are readily lost by surface runoff and also by leaching from the plant root zone into deeper soil. Other losses of these ions are due to denitrification, which is reduction to elemental nitrogen or gaseous nitrogen oxides under conditions of limited aeration. In addition to the direct economic losses, these nitrogen forms constitute environmental pollutants when runoff enters surface and ground water systems.

Although some nitrogen is applied to soil in the form of nitrate (e.g., ammonium nitrate-containing fertilizers), most nitrogen fertilization is with ammonia, ammonium compounds other than nitrate and urea materials. Ammonium nitrogen is fairly tightly bound by various physical and chemical processes in a soil environment and, therefore, is much less subject to losses. Unfortunately, the bound ammonium nitrogen is also less available to plants.
The process of nitrification results in conversion of ammonium ions into nitrate ions. Microbial species known as *nitrosomonas* oxidize ammonium to nitrate; *nitrobacter* species oxidize nitrite to nitrate. This more mobile ion is easily taken up by plant roots and is also readily assimilated by plants. In this regard, the nitrification process is desirable, but control of the rate at which conversion occurs has not been easily obtained. Inhibition of nitrification would tend to make the applied nitrogen available to plants over a longer period of time, resulting in an increased plant uptake efficiency.

Various compositions have been offered as inhibitors of nitrification, including expensive organic materials such as 2-chloro-6-(trichloromethyl)-pyridine, 2-amino-4-chloro-6-methyl-pyrimidine, sulfathiazoles, alkanoylsulfathiazoles, and others. A paper by J. M. Bremner and L. G. Bundy in *Soil Biology and Biochemistry*, Vol. 6, pages 161-165 (1974) describes the efficacy of various volatile organic sulfur compounds, including methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide, and hydrogen sulfide. Carbon disulfide in very small amounts is described as having "a remarkable inhibitory effect on nitrification of ammonium in soils incubated in closed systems." Carbon disulfide was tested in the field by J. Ashworth et al., *Chemistry and Industry*, September 6, 1975, pages 749-750, and found to be effective as a nitrification inhibitor. Hawkins, in U.S. Patent 4,078,912, describes the use of sodium, potassium and ammonium trithiocarbonates, and of xanthates, either alone or in fertilizer mixtures, to inhibit nitrifica-
tion; the mode of operation is attributed to a release of carbon disulfide by the compounds.


According to O'Donoghue and Kahan, as far back as 1826 derivatives of thiocarbonic acid were prepared by Berzelius, who reacted aqueous solutions of hydrosulfides with carbon disulfide to give unstable solutions which yielded unstable crystalline salts in accordance with the following reaction:

\[ 2 \text{KSH} + \text{CS}_2 \rightarrow \text{K}_2\text{CS}_3 + \text{H}_2\text{S} \]  (2)

Other thiocarbonates were prepared and further characterized by O'Donoghue and Kahan. Their paper, at page 1818, reports the formation of ammonium thiocarbonate by reacting liquid ammonia with cold alcoholic thiocarbonic acid prepared by dropping a solution of calcium thiocarbonate into concentrated hydrochloric acid to produce free thiocarbonic acid (H₂CS₃). The calcium thiocarbonate utilized by the authors is described as a double salt, including the calcium cation in combination with both the hydroxide and the trithiocarbonate anions. In addition to free thiocarbonic acid, other compounds prepared by O'Do-
noghu and Kahan included the sodium, potassium, zinc and lead salts. However, regardless of which of these salts were prepared, a common characteristic was their relative instability, with the prepared compounds breaking down and releasing carbon disulfide and hydrogen sulfide and/or a metal sulfide, often in a matter of minutes.

The noted paper by Yeoman reports a further study of thiocarbonates (called thithiocarbonates therein) and also reports the preparation and properties of perthiocarbonates (or tetrathiocarbonates), derivatives of tetrathiocarbonic acid ($\text{H}_2\text{CS}_4$). Yeoman reports on methods of preparing the ammonium, alkali metal and alkaline earth metal salts of these acid species. For example, Yeoman prepared ammonium trithiocarbonate by saturating an alcoholic ammonia solution with hydrogen sulfide and then adding carbon disulfide to precipitate the product salt. Ammonium perthiocarbonate was prepared in a similar manner, except that after reacting the ammonia and hydrogen sulfide, elemental sulfur was added to form the disulfide, $(\text{NH}_4)_2\text{S}_2$; adding carbon disulfide immediately precipitated the product.

Yeoman states that solutions of both ammonium trithiocarbonate and perthiocarbonate are very unstable due both to decomposition to form thiocyanate as a product, and to complete dissociation back into ammonia, hydrogen sulfide and carbon disulfide.

Considerable explanation is provided concerning the stability of thiocarbonates, as exemplified by sodium trithiocarbonate and perthiocarbonate. Sodium trithiocarbonate solutions in water are said to remain
stable only if oxygen and carbon dioxide are rigidly excluded; the presence of oxygen causes decomposition to form carbon disulfide and thiosulfates, while carbon dioxide decomposes the solution to give a carbonate and carbon disulfide. Similarly, solutions of sodium perthiocarbonate are reported to be stable for a considerable time in the absence of oxygen, the presence of air causing decomposition into thiosulfate and carbon disulfide, while carbon dioxide decomposes the compound to form a carbonate, elemental sulfur, carbon disulfide and hydrogen sulfide. The potassium thiocarbonates behave similarly, according to Yeoman.

Yeoman also attempted to prepare and characterize the stability of thiocarbonate salts of four of the alkaline earth metals. Yeoman was unable to prepare a pure calcium tri- or tetrathiocarbonate, but did observe that the double salt of calcium trithiocarbonate which he prepared was more stable (probably because it was less hygroscopic) than the sodium or potassium thiocarbonates. The barium salt of tetrathiocarbonic acid could not be isolated, although Yeoman believed it existed in solution. Solid barium trithiocarbonate could not be isolated, although it was alleged to behave like sodium trithiocarbonate when dissolved in water. The preparation of aqueous solutions of the tri- and tetrathiocarbonates of magnesium and strontium was alleged, but the magnesium thiocarbonates were not isolated.

The previously noted paper by Mills and Robinson shows the preparation of ammonium thiocarbonate by digesting ammonium pentasulfide with carbon disulfide. The ammonium pentasulfide was obtained by
suspending sulfur in aqueous ammonia, then saturating with hydrogen sulfide. A crystalline residue from the reaction was found to be ammonium perthiocarbonate. The authors prepared a "better" ammonium perthiocarbonate product, however, by extracting the ammonium pentasulfide with carbon disulfide in a Soxhlet apparatus.

Stone et al. disclose several methods for preparing solid ammonium, alkali and alkaline earth metal salts of tri- and tetraperoxythiocarbonates, hereinafter referred to simply as "tetrathiocarbonates." One such method involves the solution of an active metal such as sodium in anhydrous ethanol to form an ethoxide which, in turn, is reacted with hydrogen sulfide and carbon disulfide to form sodium trithiocarbonate. They report, however, that the trithiocarbonates tend to be quite soluble in ethanol, and if it is desired to recover the solid material from the solution, it is necessary to treat the reaction mixture with a "displacing agent" such as ether, in which case the thiocarbonates frequently separate, not as solids, but as difficultly crystallizable oils which appear to be saturated aqueous solutions of the trithiocarbonate salt. Consequently, such a procedure is not considered feasible for use on a commercial scale. Similar problems were reported with tetrathiocarbonate salts, which were prepared using procedures analogous to those for the trithiocarbonates.

These problems were reportedly solved by carrying out the preparation reaction in a medium which is composed of a major part of a nonsolvent for the reaction components and a minor proportion of a liquid
which is miscible with the nonsolvent and which is a solvent, to a measurable degree, for inorganic sul-
fides. The preferred nonsolvents used were relatively low boiling hydrocarbon materials such as hexane, cyclohexane and benzene. The second solvent was preferably ethanol, isopropanol or dioxane.

Basic physical and chemical properties of these materials and a number of methods for making them are summarized in considerable detail, at pages 154-177 in "Carbon Sulfides and their Inorganic and Complex Chemistry" by G. Gattow and W. Behrendt, Volume 2 of "Topics in Sulfur Chemistry", A. Senning, Editor, George Thieme Publishers, Stuttgart, 1977.

SUMMARY OF THE INVENTION

The present invention provides a process for the production of salts of thiocarbonic acids in solid form, stabilized thiocarbonates and methods for their use.

According to the present invention stabilized aqueous solutions of thiocarbonate salts are converted to solid thiocarbonates by evaporating to dryness. Such stabilized aqueous solutions are described in copending applications Serial Nos. 07/262,961, filed October 28, 1988, 07/262,962, filed October 28, 1988, 07/415,874, filed February 10, 1989 and 07/440,024, filed November 21, 1989, the disclosures of which in their entireties are incorporated herein by reference, in which a sulfide, polysulfide and/or base are used to stabilize the thiocarbonate solution.

Water is evaporated from an aqueous solution
of a salt of the desired trithiocarbonic acid or tetra-
thiocarbonic acid containing a stabilizing amount of a
sulfide, polysulfide and/or base. Preferably a stabi-
lizing amount of a sulfide or polysulfide is used.
More preferably a stabilizing amount of a base is used
with the sulfide or polysulfide. Evaporation can be
accomplished by boiling the solution under vacuum or
evaporating at ambient pressures and sub-boiling tem-
peratures. Typically, a wet solid is produced and the
wet solid is then further dried at elevated tempera-
tures to produce the desired essentially dry solid
product. In an especially preferred embodiment the two
steps are combined in a semi-continuous process.

The desirability of using solid thiocarbonate
salts stems from the fact that, in addition to being
more easily handled and transported, the rate of re-
lease of CS$_2$ from the solid salts can be readily manip-
ulated by various methods such as coating the solid
salt or mixing with adjuvants. Unlike aqueous solu-
tions of thiocarbonate salts, which are used principal-
ly by adding the solutions to water used for spraying
or irrigation, solid thiocarbonate salts are advanta-
geous for use in dry farming. Thus, a solid thiocar-
bonate applied to dry soil will release CS$_2$ upon con-
tact with water, for example rain.

A particular advantage of the process of the
present invention is that the previously available
methods of producing solid thiocarbonate salts required
the use of organic solvents, the disposal of which
presented environmental problems. The present inven-
tion, on the other hand, requires no organic solvents
and presents no disposal problems. A further advantage
is that the "stabilized" solid thiocarbonates obtained by the described methods are more stable than the solids obtained by previous investigators, and they are therefore more useful as fumigants, intermediates for the manufacture of other thiocarbonate-containing compositions, and for the manufacture of "stabilized" thiocarbonate solutions, such as those described in copending applications Serial Nos. 07/262,961 and 07/262,962, supra, upon dissolution in water.

**BRIEF DESCRIPTION OF THE DRAWING**

The sole figure of the drawing is a schematic representation of a flowsheet in partial elevation showing a system for conducting the process of the present invention.

**DETAILED DESCRIPTION**

Although aqueous solutions of thiocarbonates are useful for various commercial applications, such as in the control of nematodes and other soil-borne and water-borne plant pathogens, the use of thiocarbonate solutions has several disadvantages. Because aqueous solutions of thiocarbonates break down upon exposure to air, elevated temperatures or a low pH environment, the solutions must be kept tightly covered during handling prior to use. In addition the solutions have a relatively short half-life after application to the soil.

It would be desirable to furnish thiocarbonates in a form which could be more easily handled and
used than aqueous solutions. We have also found that it is desirable to provide a method for the manufacture of solid thiocarbonates which does not require the use of solvents other than water and that is capable of producing "stabilized" thiocarbonates which are more stable than solid thiocarbonates available in the prior art, e.g. such as those disclosed by Mills and Robinson and Stone et al. both supra. Furthermore, such "stabilized" solid thiocarbonates are more suitable for a variety of uses including their use as space and soil fumigants for the control of plant pests and insect and animal pests that consume and/or adulterate stored food products or other materials. Also, the "stabilized" solid thiocarbonates described herein are more suitable than the solid thiocarbonates previously available as intermediates for the manufacture of other materials such as the stabilized solid thiocarbonate compositions disclosed by Pilling and Young in copending application Serial No. 07/290,992, filed December 28, 1988, the disclosure of which is incorporated herein by reference in its entirety.

The stabilized, aqueous thiocarbonate solutions from which the stabilized solids can be derived involve aqueous solutions of thiocarbonates, soluble in the solution and having the general formula \[ A_aCS_b \]
wherein \( A \) is a mono- or divalent cation, \( b \) is 3 to 4, \( a \) is 2 when \( A \) is a monovalent cation, and \( a \) is 1 when \( A \) is a divalent cation, and a base and/or a sulfide and/or polysulfide of the formula \( M_nS_x \) wherein \( M \) is selected from mono- and divalent cations, and combinations thereof, \( x \) is at least 1, \( n \) is 2 when \( M \) is a monovalent cation, and \( n \) is 1 when \( M \) is a divalent
cation. The aqueous solutions can comprise mixtures of tri- and tetrathiocarbonates having the same or different cations as well as mixtures of sulfides and polysulfides of the same or different cations. Due to ready availability and relatively low cost, the thiocarbonates presently preferred are the ammonium and alkali and alkaline earth metal thiocarbonates and combinations of these, with the alkali and alkaline earth metal thiocarbonates being the most preferred.

The "stabilized solid" thiocarbonates are "non-stoichiometric" in that they contain excess, equivalent base and/or sulfide and that they are more stable upon exposure to water, air and/or elevated temperatures than are solids prepared from aqueous or non-aqueous media and "stoichiometric" thiocarbonate compositions, i.e. compositions comprising only amounts of carbon, sulfur and cation corresponding to the empirical formula for the corresponding tri- and/or tetrathiocarbonates in the absence of significant amounts of excess base and/or sulfide. Typically, the stabilized, solid thiocarbonates are stable in air at 24°C and 50 percent relative humidity for at least about 30 minutes, generally at least about 1 hour, preferably at least about 2 hours and most preferably at least about 6 hours, stability being determined by the time required for the thiocarbonate to lose 50 percent of the equivalent CS₂ contained in the original solid. There is a decreased tendency of the stabilized, solid thiocarbonates to absorb water from the atmosphere, deliquesce and oxidize as do the unstabilized solids not containing excess base and/or sulfide. Decreased moisture absorption is reflected in higher,
critical relative humidity for the stabilized solids of typically at least about 10 percent, generally at least about 35 percent, preferably at least about 50 percent and most preferably at least about 90 percent. Critical relative humidity is the relative humidity of the ambient air below which the solid will not absorb water from the environment. The stability of the solids in air at the selected relative humidity and temperature can be readily determined by screening the solids to obtain particles passing 30 U.S. standard mesh and letting those particles stand under the designated conditions until a characteristic color change (to white) occurs, for a designated period of time, or until a specified amount of equivalent CS$_2$ has been lost to the atmosphere. CS$_2$ loss can be determined by capturing the vapor phase overlying the solid and analyzing it for carbon disulfide. Similarly, the amount of equivalent CS$_2$ remaining in the solid after the foregoing stability test can be determined by dissolving the remaining solid in water, acidifying to a pH of about 4 or less to decompose the thiocarbonate, and capturing the resulting CS$_2$ released in a toluene phase overlying the water phase in which the thiocarbonate is dissolved. The evolved CS$_2$ is captured in the toluene phase, and its concentration can be determined by analyzing the toluene phase for CS$_2$ by gas chromatography.

The stabilized solids can also be characterized by composition, i.e. the amount of equivalent base, sulfide and/or polysulfide in excess of the stoichiometric composition of the thiocarbonate. The amount of excess base, sulfide and/or polysulfide will
usually correspond to at least about 0.01, typically at least about 0.02, preferably at least about 0.04 and most preferably at least about 0.08 equivalent of base, sulfide or polysulfide per equivalent of carbon disulfide in the solid thiocarbonate.

In addition to the several advantages of the stabilized, solid thiocarbonates discussed herein, they have the further advantage that, when dissolved in water, they form stabilized, thiocarbonate solutions such as those disclosed in copending applications Serial Nos. 07/262,961 and 07/262,962. As disclosed in those copending applications, stabilized, aqueous solutions of thiocarbonates containing excess base, sulfide and/or polysulfide are much more resistant to thiocarbonate decomposition and are therefore more useful as fumigants, intermediates, and in other industrial applications.

The resulting, stabilized, solid thiocarbonates can be used directly as such or can be dissolved in water or solvents other than water for use in agriculture or industrial applications where thiocarbonates are useful or required. Thus the solids, or solutions derived therefrom, can be employed as fumigants for enclosed spaces, stored grains or other perishables, soil fumigants for the control of plant pathogens and vectors, e.g. nematodes, insects, fungi, bacteria, viruses, et cetera, or may be applied to the foliage of plants, the soil surface or to other areas for the control of pests of all varieties. They may be applied to soils or fertilizer compositions to inhibit nitrification of ammoniacal fertilizers as disclosed in copending application Serial No. 07/128,146, for the
dissolution of paraffinic and/or bituminous deposits and for reducing the pour point of hydrocarbons/petroleum as disclosed in copending application Serial No. 07/222,801 and for the manufacture of extreme pressure lubricants as disclosed in copending applications Serial Nos. 07/253,139 and 07/260,912. The disclosures of the four referenced patent applications are incorporated herein by reference in their entireties.

In the process of the present invention, a stabilized, aqueous solution of a thiocarbonate salt is converted to a solid thiocarbonate salt by a process which involves removing the water from a stabilized, aqueous, thiocarbonate salt solution. Since thiocarbonate salt solutions break down upon exposure to excessively elevated temperatures, it is not possible merely to evaporate a thiocarbonate salt solution to dryness at any elevated temperature. Moreover, it is difficult and generally not possible to evaporate a stoichiometric thiocarbonate solution to dryness, since CS$_2$ will be released and the typical product will be an oil rather than the desired solid. Consequently, it is necessary to stabilize the solution by the use of sulfides, polysulfides or bases, as will be explained in detail in the ensuing description.

The term "stability", as used herein with regard to the aqueous solutions, can be regarded as a composite of two concepts: chemical stability and physical stability. Since the effectiveness of a composition depends, at least in part, upon its ability to release carbon disulfide during decomposition, chemical stability is expressed accordingly: this can be quantified by, for example, chemically decomposing
the composition and measuring the amount of carbon disulfide which evolves. Alternatively, an indication of the amount of available carbon disulfide can be obtained by spectrophotometrically determining the presence of the thiocarbonyl bond (C=S) in a sample of the composition. The absorbance at wavelengths corresponding to those at which thiocarbonyl is known to absorb energy can be used for a quantitative analysis.

Symptomatic of chemical stability, but having an independent significance, is physical stability. This concept is important due to the nature of the products formed during decomposition of the composition, particularly the ammonia (when present), hydrogen sulfide, and carbon disulfide, which each have a high vapor pressure. It is readily apparent that a change in the physical form of the composition from a solution of low vapor pressure into a mixture of compounds, each possessing a high vapor pressure, imposes some rather stringent requirements upon storage containers. Vapor pressure above the composition of the invention, therefore, will be used herein as an indicator of physical stability; a condition of maintained low vapor pressure is the desired property. Another index of physical instability is the formation of undesirable insoluble precipitates, which frequently comprise sulfur, or of an immiscible liquid phase, such as carbon disulfide. The more general description of physical stability, then, is the maintenance of only a single phase in the composition.

Assessment of the stability of a particular solution usually involves consideration of both the
chemical stability and the physical stability over a period of time during which stability is desired. Certain formulations do not form precipitates and do not develop high vapor pressures during a reasonable storage period and, therefore, may be preferred over a formulation which has a greater chemical stability, but develops objectionable physical characteristics during storage.

The useful thiocarbonates include, without limitation, salts of trithiocarbonic acid and tetrathiacarbonic acid, compositions having empirical formulae intermediate to these acid salts (such as $\text{MCS}_3$,$^7_7$, wherein $\text{M}$ is a divalent metal ion), and compositions containing substances in addition to thiocarbonates, such as a stabilized ammonium tetrathiocarbonate which contains ammonium sulfide, i.e., $(\text{NH}_4)_2\text{CS}_4\cdot(\text{NH}_4)_2\text{S}$. These compositions are generally water soluble and can be prepared, stored, and used in aqueous solutions. The solutions are stable during prolonged periods of storage in a closed container, exhibit low vapor pressure, and are not flammable.

The stability of both the concentrated and dilute thiocarbonate solutions can be markedly increased, with respect to $\text{CS}_2$ evolution and physical stability, by the addition of a base, sulfide and/or polysulfide. Increases in stability are particularly evident in the more concentrated solutions, i.e. solutions having equivalent $\text{CS}_2$ concentrations in excess of 1 weight percent. Aqueous solutions that can be stabilized by the addition of base, sulfide and/or polysulfide include solutions of alkali, alkaline earth and ammonium tri- and tetrathiocarbonates and combinations
of these, and very stable alkali metal and alkaline earth metal tetrathiocarbonate solutions can be obtained. Significant stability enhancement can be achieved even in the most concentrated solutions. Thus, significant stability enhancement can be achieved in compositions having equivalent CS$_2$ concentrations of about 1 weight percent or more or even 5 weight percent or a more equivalent CS$_2$ up to the solubility limit of the thiocarbonate in the solution. Typically, the more concentrated solutions have thiocarbonate concentrations corresponding to about 1 to about 20 weight percent equivalent carbon disulfide. The stability and safety of concentrates containing 10 weight percent or more equivalent CS$_2$ can be markedly improved by these procedures.

Stability enhancement can be achieved by providing, in the solution, an organic or inorganic base which, preferably, is soluble in the solution, and more preferably, has significant solubility in water. Presently preferred bases include water-soluble inorganic bases, and the most preferred, are alkali metal and ammonium hydroxides, and combinations of these. Alternatively, similar increases in stability can be achieved by providing, in the solution, a sulfide and/or polysulfide which, preferably, is soluble in the solution, and more preferably, has significant solubility in water. Illustrative sulfides include ammonium, alkali and alkaline earth metal sulfides and polysulfides having the general, empirical formula $M_nS_x$, wherein M is ammonium, alkali or alkaline earth metal, x is at least about 1, preferably greater than 1 in the case of polysulfides, and usually within the range of 1
to about 5, most preferably greater than 1 to about 5, n is 2 when M is ammonium or alkali metal, and n is 1 when M is an alkaline earth metal. Combinations of different sulfides and/or polysulfides can be employed. Thus, combinations of ammonium, alkali and/or alkaline earth metal sulfides and/or polysulfides can be used to stabilize the thiocarbonate compositions, and combinations of the described bases, sulfides and/or polysulfides can be used to achieve further enhanced stability, and are presently preferred. Presently, the most preferred stabilized, thiocarbonate solutions contain added base in addition to one or more of the described sulfides or polysulfides.

Any amount of added base or sulfide, or combination of these, enhances the solution's stability. Thus, the useful compositions comprise aqueous solutions of thiocarbonates containing added base, sulfide and/or polysulfide. Generally, the amount of added base, sulfide or polysulfide will correspond to about 0.01, usually about 0.02, preferably at least about 0.04, and most preferably about 0.08 equivalents of base, sulfide or polysulfide per equivalent of carbon disulfide in the solution. Concentrated, aqueous tetrathiocarbonate solutions having CS₂ vapor pressures corresponding to CS₂ concentrations in the equilibrium vapor phase below about 1 volume percent at 24₀ C. (75₀ F.), i.e. below the explosive limit for carbon disulfide, can be achieved with base concentrations of about 0.02 equivalent of base per equivalent of carbon disulfide. Somewhat higher base concentrations, i.e. at least about 0.08 equivalents of base per equivalent of carbon disulfide, are presently preferred.
for producing aqueous, trithiocarbonate solutions having CS$_2$ partial pressure corresponding to about 1 volume percent or less carbon disulfide in the equilibrium vapor phase at 24° C. (75° F.). While significant improvements in solution stability and reductions in CS$_2$ partial pressure can be achieved by the use of sulfides and/or polysulfides in the absence of added base, the concentration of sulfide and/or polysulfide required to achieve the desired reduction in CS$_2$ partial pressure (and consequent increase in stability) is generally somewhat higher than the concentration of base required to achieve a similar stability improvement. Thus, in order to obtain a CS$_2$ partial pressure corresponding to a CS$_2$ concentration in the equilibrium vapor phase overlying the solution below 1 volume percent at 24° C., it is presently preferred to employ concentrations of sulfide and/or polysulfide of about 0.04 or more equivalent of sulfide and/or polysulfide per equivalent of carbon disulfide. As in the case of added base, greater solution stability and lower CS$_2$ partial pressures can be achieved by using even higher concentrations of sulfides and/or polysulfides, or by employing combinations of base and sulfide and/or polysulfide. Typically, the concentration of sulfide, polysulfide or combination thereof will correspond to at least about 0.02, preferably at least about 0.04, and most preferably at least about 0.08 equivalent of sulfide and/or polysulfide per equivalent of carbon disulfide. However, when combinations of base and sulfide are employed, the respective concentrations of each can be reduced by approximately 1/2 to obtain a comparable degree of stability improvement and CS$_2$
partial pressure reduction. In other words, the degree of stability enhancement achieved by the use of 0.02 equivalent of base per equivalent of carbon disulfide, can be achieved by using approximately 0.01 equivalent of base in combination with about 0.01 equivalent of sulfide or polysulfide. The term "equivalent," as employed herein, is used in its conventional sense. Thus, one mole of carbon disulfide constitutes 2 equivalents, and the same is true for the sulfide and polysulfide and for the alkaline earth metal bases and other bases which can be employed in which the cation is divalent. However, one mole of the ammonium and alkali metal bases, wherein the cation is monovalent, constitute only 1 equivalent. Therefore, on a molar basis, as opposed to an equivalent basis, 2 moles of an alkali metal hydroxide, e.g. sodium hydroxide, are equivalent to 1 mole of carbon disulfide.

Accordingly, the amount of base, sulfide and/or polysulfide employed should be sufficient to reduce the carbon disulfide partial pressure of the solution by the desired amount, and the amount of additive required to achieve that effect can be easily determined by adding different, known quantities of base, sulfide and/or polysulfide to the desired thio-carbonate solution, confining the vapor space over the solution at 24° C. for a sufficient period of time, e.g. about 24 hours, and analyzing the vapor phase by gas chromatography for carbon disulfide. Lower additive concentrations will result in somewhat higher CS₂ equilibrium concentrations (e.g. higher CS₂ partial pressures), and higher additive concentrations will result in lower CS₂ partial pressures.
The most preferred compositions, presently, are those in which the carbon disulfide partial pressure has been reduced to a level corresponding to about 1 volume percent or less carbon disulfide in the equilibrium vapor phase at 24°C. A greater safety factor, with regard to CS₂ partial pressure, toxicity, handling difficulty, etc., can be realized by reducing CS₂ partial pressure even further. Thus, more preferred thiocarbonate solutions are those in which the carbon disulfide partial pressure corresponds to less than about 0.5, most preferably less than about 0.2 volume percent carbon disulfide in the equilibrium vapor phase overlying the solution at 24°C.

Base-containing compositions of enhanced stability can be readily obtained by providing the desired amount of base in the thiocarbonate salt solution. Base can be introduced before, during or after preparation of the thiocarbonate salt solution, it being necessary only that the final composition contain additional base. Preferably, such added base is provided either during or after preparation of the thiocarbonate salt solution. Similar techniques can be employed to prepare sulfide- and polysulfide-containing compositions. Thus, soluble sulfide or polysulfide can be introduced before, during or after preparation of the thiocarbonate salt solution, although sulfides are preferably added either during or after preparation of the thiocarbonate salt solutions. Sulfide and polysulfide can be provided in the composition by direct addition of such compounds, or they can be formed in situ. Thus, an amount of base, for example, potassium hydroxide, can be added followed by addition of an equivalent
quantity of hydrogen sulfide to convert the base to the corresponding sulfide, potassium sulfide (K₂S). The polysulfides can be formed in situ by addition of elemental sulfur with adequate agitation to promote the reaction of the elemental sulfur with the sulfide already present in the composition.

The present process removes water from the aqueous, thiocarbonate salt solution which has been stabilized against loss of CS₂. Water is removed by treatment at temperatures which result in the evaporation of water from the solution without excessive decomposition of the thiocarbonate salt, which decomposition results in the loss of CS₂ from the salt. Such process is conducted by evaporating the stabilized, thiocarbonate salt solution at temperatures below the boiling point of the solution or by boiling the stabilized, thiocarbonate salt solution under sufficient vacuum to ensure that significant decomposition does not occur.

Any evaporation process or vacuum distillation process which meets these requirements is satisfactory for the purposes of this invention. Typically, vacuum evaporation is used for evaporation of water from a stabilized aqueous solution of a thiocarbonate since thiocarbonates are subject to decomposition at relatively low temperatures. However, any procedure can be employed which results in the formation of a dried thiocarbonate containing a significant amount of bound CS₂. Thus, the stabilized, aqueous solution can be evaporated at ambient temperatures and pressures by simply allowing water to evaporate from the solution into the air. A vacuum can be drawn on the solution
and/or the solution can be heated to a temperature that does not result in excessive thiocarbonate decomposition. "Excessive thiocarbonate decomposition" as used herein means such extensive decomposition of the thiocarbonate initially present in the stabilized solution that an insignificant amount of solid thiocarbonate is recovered as a result of the evaporation procedure.

The invention will be described with reference to producing a solid potassium tetrathiocarbonate product. Other thiocarbonates can be used as well. The decomposition point of solid potassium thiocarbonate determined in a melting point apparatus is about 302° F. The boiling point of aqueous solutions of thiocarbonates varies depending upon the concentration and pressure. For example, a 40 weight percent solution of potassium thiocarbonate boils at about 155° F. under a vacuum of about -25 inches Hg whereas the boiling point at atmospheric pressure is about 215° F. In general, the boiling point at atmospheric pressure is about 60° F. higher than under a vacuum of -25 inches Hg. An 80 weight percent oily solution of the salt boils at about 195° F. under a vacuum of -25 inches Hg and at about 255° F. at atmospheric pressure. Distilling off the water from a solution of potassium thiocarbonate under a vacuum of about -25 inches Hg causes the temperature to slowly rise to about 200° F. as the vacuum distillation proceeds. At this point a solid begins to separate from the solution. The solid which is formed is moist to the touch and has a tendency to cake.

Drying to produce a non-caking solid can be accomplished at ambient pressure using a rotary dryer,
a spray dryer, an evaporator or a low temperature kiln.
A dry solid is produced at ambient pressure with the
temperature rising from about 270° F. to about 290° F.
The potassium tetrathiocarbonate begins to decompose at
temperatures over about 300° F.

Drying under a vacuum of about -25 inches Hg
or lower is preferred, because by drying a stabilized
aqueous thiocarbonate salt solution under a vacuum a
dry solid thiocarbonate salt is produced at tempera-
tures substantially below the decomposition temperature
of the salt. At -25 inches Hg vacuum, for example, a
dry solid is formed at a temperature of about 210° F.
to about 230° F. Drying under a vacuum is typically
accomplished by using a Sigma blades mixer, a ribbon
mixer or a rotary mixer.

The process of the present invention will be
better understood by reference to the drawing which
illustrates a system for producing solid thiocarbonate
salts in a batchwise or semi-continuous manner.

A liquid storage tank 10 is connected to a
feed pump 12 by means of a conduit 14. Feed pump 12 is
connected to a liquid distributor 16 by means of a
conduit 18. Liquid distributor 16 is disposed within
and is part of rotary dryer 20 which is equipped with a
heating jacket 22. Rotary dryer 20 is connected to a
heat exchanger 24 which functions as a condenser by
means of a conduit 26. A vacuum receiver 28 is con-
ected to heat exchanger 24 by means of a conduit 30.
A condensate pump 32 is connected to vacuum receiver 28
by means of a conduit 34. A gas blower 36 is connected
to vacuum receiver 28 by means of a conduit 38 equipped
with a valve 40. Gas blower 36 is connected to a
vacuum pump, not shown, by means of a valve 42 and a conduit 44. Gas blower 36 is bypassed by means of a conduit 46 equipped with a valve 48. Gas blower 36 is also connected to another valve 50 which is connected to a gas heater 52 by means of a conduit 54 and to a valve 56 in a conduit 58 which connects with an inert gas supply, not shown. Gas heater 52 is connected to a gas inlet 60 of rotary dryer 20 by means of a conduit 62. Rotary dryer 20 is adapted to rotate in the direction shown by arrow 64. Alternatively, rotary dryer 20 can be replaced with a stationary vessel equipped with internal, rotating mixing elements, if desired. A gas outlet 66 of rotary dryer 20 is connected to conduit 26. Within rotary dryer 20 are shown liquid sprays 68 exiting from liquid distributor 16, solid product 70 and grinding media 72 shown intermixed with solid product 70.

Starting materials for the process of the present invention are typically thiocarbonate salt solutions having concentrations of about 15 to about 80 weight percent thiocarbonate and preferably concentrations of about 30 to about 60 weight percent. Although potassium tetrathiocarbonate has been mentioned specifically, it should be understood that other thiocarbonates such as ammonium trithiocarbonate and tetrathiocarbonate and other alkali metal and alkaline earth metal thiocarbonate salts as well as other metal salts of thiocarboxylic acids can be similarly processed to provide solid thiocarbonates.

In order to ensure that the aqueous thiocarbonate salt solution being evaporated will not release excessive quantities of CS₂ and will instead release
primarily water vapor, it has been found advantageous to provide a stabilized aqueous solution. Stabiliza-
tion can be accomplished by including with the thiocar-
bonate a base, a soluble sulfide salt or a polysulfide.

The use of excess quantities of sulfide and base during the preparation of aqueous thiocarbonate salt solutions is described in copending applications Serial Nos. 415,874 and 440,024.

In carrying out the process of the present invention as a batch process, the stabilized aqueous thiocarbonate salt solution, exemplified herein as K₂CS₄, is pumped from liquid storage tank 10 and sprayed into rotary dryer 20 by means of liquid distributor 16. Rotary dryer 20 is maintained at the desired temperature by means of heating jacket 22 which increases and controls the temperature of the K₂CS₄ solution in the rotary dryer. During the evaporation and drying process water vapor from the K₂CS₄ solution is condensed in the heat exchanger 24 through the conduit 30 to the vacuum receiver 28 to be disposed of by means of condensate pump 32. Any noncondensible gas or gases evolved is bypassed around gas blower 36 through conduit 38, conduit 46 and valve 48, which is open, to valve 42, which is also open and thence to the vacuum pump for disposal. Valves 40, 50 and 56 are closed during this batch process.

During the evaporating and drying process, the rotary dryer is rotated in the direction shown by arrow 64. The grinding media, shown as grinding media 72 in the drawing, which are optional, are typically ceramic balls or alloy steel balls which are added to prevent caking or sticking of the solid product on the
walls of rotary dryer 20. If desired, internal wipers or blades, not shown, can be used to maintain the heat transfer surface of rotary dryer 20 or an alternative stationary vessel free of solids.

Instead of the vacuum evaporation and drying process described above a process which utilizes an inert gas such as nitrogen as the heating medium can be used. In this process the stabilized aqueous thiocarbonate salt solution, exemplified herein as $K_2CS_4$, is pumped from liquid storage tank 10 and sprayed into rotary dryer 20 by means of liquid distributor 16. Rotary dryer 20 is maintained at the desired temperature by means of heating jacket 22 and gas heater 52, which control the temperature of the inert gas entering rotary dryer 20 through gas inlet 60. The rate at which the solution is sprayed into the rotary dryer also controls the rate of evaporation of the water from the solution and the rate of deposition of solid on the accumulating bed of solids within the rotary dryer. The inert gas supply not only prevents unwanted oxygen from entering the rotary dryer, but also serves to sweep the water vapor from the dryer through gas outlet 66 and conduit 26 to heat exchanger 24. Water vapor released from the $K_2CS_4$ solution during the evaporation and drying process is condensed in heat exchanger 24 and passed through conduit 30 to vacuum receiver 28 to be disposed of by means of condensate pump 32. The inert gas is passed through gas blower 36 and valve 50, and is recycled to gas heater 52. Valves 42, 48 and 56 are closed during this process. Additional inert gas can be supplied through valve 56 if required.

A combination of the above two processes is
also desirable. In such a process vacuum is used to evaporate the water vapor from the thiocarbonate solution and inert gas is later used to dry the solid.

The solid thiocarbonate salts produced according to the present invention may be somewhat hygroscopic. In that event, and particularly under conditions of high humidity, the solid products are preferably packed in appropriate containers and sealed after drying.

The present invention thus provides a process for producing solid salts of thiocarbonic acids conveniently without utilizing organic solvents and without causing decomposition of the thiocarbonate salts.

The invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. For example, as pointed out above, other devices than a rotary dryer can be used to evaporate water from the aqueous thiocarbonate solutions used as starting materials in the process of the present invention. Consequently, the present embodiments are to be considered only as being illustrative and not restrictive, with the scope of the invention being indicated by the appended claims. All embodiments which come within the scope and equivalency of the claims are therefore intended to be embraced therein.
We claim:

1. A process for the production of a solid salt of a thiocarbonic acid which comprises evaporating a stabilized aqueous solution of a salt of a thiocarbonic acid to dryness.

2. A process according to claim 1 wherein said salt is a member of the group consisting of ammonium trithiocarbonates, ammonium tetrathiocarbonates, alkali metal trithiocarbonates, alkali metal tetrathiocarbonates, alkaline earth metal trithiocarbonates and alkaline earth metal tetrathiocarbonates.

3. A process according to claim 1 wherein said solution has a concentration of about 15 to about 80 weight percent of said salt.

4. A process according to claim 1 wherein said solution has a concentration of about 30 to about 60 weight percent of said salt.

5. A process according to claim 1 wherein said solution contains a stabilizing amount of a member selected from the group consisting of sulfides, polysulfides, bases and mixtures thereof.

6. A process according to claim 5 wherein said stabilizing amount is at least about 0.01 equivalent per equivalent of carbon disulfide present in said salt.

7. A process according to claim 5 wherein
said stabilizing amount is at least about 0.08 equivalent per equivalent of carbon disulfide present in said salt.

8. A process according to claim 2 wherein said solution contains a stabilizing amount of a member selected from the group consisting of sulfides, polysulfides, bases and mixtures thereof.

9. A process according to claim 4 wherein said solution contains a stabilizing amount of a member selected from the group consisting of sulfides, polysulfides, bases and mixtures thereof.

10. A process for the production of a solid salt of a thiocarbonic acid which comprises evaporating a stabilized aqueous solution of a salt of a thiocarbonic acid to remove water from said solution and drying the solid resulting from said evaporating step, said solution being stabilized with a stabilizing amount of a member selected from the group consisting of sulfides, polysulfides, bases and mixtures thereof.

11. A process according to claim 10 wherein said solution contains a stabilizing amount of a mixture of a sulfide or polysulfide and a base.

12. A process according to claim 10 wherein said stabilizing amount is at least about 0.01 equivalent per equivalent of carbon disulfide present in said salt.
13. A process according to claim 10 wherein said stabilizing amount is at least about 0.08 equivalent per equivalent of carbon disulfide present in said salt.

14. A process according to claim 10 wherein said evaporating step is carried out by boiling said solution under vacuum.

15. A process according to claim 10 wherein said evaporating step is carried out at ambient pressure at a sub-boiling temperature.

16. A process according to claim 10 wherein said drying step is carried out by heating said resulting solid at an elevated temperature.

17. A process according to claim 16 wherein said elevated temperature is a temperature higher than ambient temperature but lower than the decomposition temperature of said salt.

18. A process according to claim 10 wherein said evaporating step and said drying step constitute a semi-continuous process.

19. A process according to claim 10 wherein said evaporating step is carried out under vacuum and said drying step is carried out under ambient pressure.

20. A process according to claim 10 wherein said evaporating step and said drying step are carried
out under vacuum.

21. A process according to claim 12 wherein said evaporating step and said drying step are carried out under ambient pressure.

22. A process according to claim 14 wherein said vacuum is at least about -25 inches Hg.

23. A process according to claim 19 wherein said vacuum is at least about -25 inches Hg.

24. A process according to claim 20 wherein said vacuum is at least about -25 inches Hg.

25. A process according to claim 1 wherein said salt is potassium tetrathiocarbonate.

26. A process according to claim 5 wherein said salt is potassium tetrathiocarbonate.

27. A process according to claim 7 wherein said salt is potassium tetrathiocarbonate.

28. A process according to claim 10 wherein said salt is potassium tetrathiocarbonate.

29. A process according to claim 13 wherein said salt is potassium tetrathiocarbonate.

30. A process according to claim 1 wherein said solution has a $\text{CS}_2$ partial pressure corresponding
to less than about 1 volume percent CS₂ in the equilibrium vapor phase at 75⁰ F.

31. A process according to claim 1 wherein said solution has a CS₂ partial pressure corresponding to less than about 0.2 volume percent CS₂ in the equilibrium vapor phase at 75⁰ F.

32. A process according to claim 10 wherein said solution has a CS₂ partial pressure corresponding to less than about 1 volume percent CS₂ in the equilibrium vapor phase at 75⁰ F.

33. A process according to claim 10 wherein said solution has a CS₂ partial pressure corresponding to less than about 0.2 volume percent CS₂ in the equilibrium vapor phase at 75⁰ F.

34. A process for the production of a solid salt of a thiocarbonic acid which comprises evaporating a stabilized aqueous solution of a salt of a thiocarbonic acid selected from the group consisting of ammonium trithiocarbonates, ammonium tetrathiocarbonates, alkali metal trithiocarbonates, alkali metal tetrathiocarbonates, alkaline earth metal trithiocarbonates and alkaline earth metal tetrathiocarbonates, having a concentration of about 30 to about 60 weight percent of said salt, said solution being stabilized with at least about 0.01 equivalent of a member selected from the group consisting of sulfides, polysulfides, bases and mixtures thereof per equivalent of carbon disulfide.
present in said salt, said solution having a CS₂ partial pressure of less than about 1 volume percent CS₂ in the equilibrium vapor phase at 75⁰ F., to remove water from said solution, and drying the solid resulting from the evaporating step.

35. A process according to claim 34 wherein said evaporating step and said drying step are carried out at ambient pressures.

36. A process according to claim 34 wherein said evaporating step and said drying step are carried out under a vacuum of at least about -25 inches Hg.

37. A stabilized, solid thiocarbonate as prepared by the method defined in claim 10.

38. A stabilized, solid thiocarbonate having the empirical formula AₐCSₙ and a stabilizing amount of a member selected from the group consisting of bases, sulfides, polysulfides and combinations thereof, wherein A is selected from mono- and divalent cations, b is 3 to 4, a is 2 when A is a monovalent cation, and a is 1 when A is a divalent cation.

39. A method for controlling pests which comprises applying to the vicinity occupied or traversed by said pests a composition comprising the stabilized, solid thiocarbonate defined in claim 37.

40. A method for controlling pests which comprises applying to the vicinity occupied or tra-
versed by said pests a composition comprising the stabilized, solid thiocarbonate defined in claim 38.

41. A method for controlling pests in soils which comprises applying to said soil a composition comprising the stabilized, solid thiocarbonate defined in claim 37.

42. A method for controlling pests in soil which comprises applying to said soil a composition comprising the stabilized, solid thiocarbonate defined in claim 38.
**INTERNATIONAL SEARCH REPORT**

**International Application No.** PCT/US 91/01325

I. CLASSIFICATION OF SUBJECT MATTER

(if several classification symbols apply, indicate all)6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C01D13/00 ; C01C1/28 ; C01F11/00 ; A01N25/18

II. FIELDS SEARCHED

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Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched8

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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* Special categories of cited documents: 

- "A": document defining the general state of the art which is not considered to be of particular relevance.
- "E": earlier document but published on or after the international filing date.
- "I": document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified).
- "O": document referring to oral disclosure, use, exhibition or other means.
- "P": document published prior to the international filing date but later than the priority date claimed.

"T": later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.

"X": document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step.

"Y": document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A": document member of the same patent family.

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 6

Date of Mailing of this International Search Report: 11/07/91

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: VAN BELLINGEN I.
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US9101325
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 20/06/91

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