

## UNITED STATES PATENT OFFICE

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TETRACHLOROETHYLENE STABILIZED BY  
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corporation of DelawareNo Drawing. Application May 18, 1950,  
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This invention relates to inhibiting the decomposition of tetrachloroethylene catalyzed by light, air, heat, moisture, and metal surfaces and more particularly relates to a composition of matter consisting essentially of tetrachloroethylene and stabilizing amounts of a compound of the group of 2-chlorothiophene and 2-bromothiophene.

It has heretofore been known that tetrachloroethylene (perchloroethylene) of a high degree of purity and containing only minute amounts of saturated, or other unsaturated, lower aliphatic chloro-hydrocarbons is very inert to the action of air, light, heat, moisture, and metal surfaces with which it comes into contact during storage and commercial use. However, the obtaining of such high purity tetrachloroethylene in commercial production is not generally feasible and it has been found that the impure material normally encountered in commerce decomposes when in contact with the substances noted above. Hence, means other than purification for preventing or inhibiting the decomposition of tetrachloroethylene and the lower chlorinated aliphatic hydrocarbons generally associated therewith must be had.

It is generally believed that tetrachloroethylene exposed to air, light, heat, moisture, etc., decomposes, especially in the presence of moisture, principally by way of oxidative attack at the double bond involving a series of steps in which the ultimate products include phosgene, trichloroacetic acid, and hydrogen chloride. It is also believed that the oxidative attack is catalyzed by light and by the products of oxidation, as a result of which, oxidative decomposition once initiated is self-catalyzing and self-sustaining. Other chloro-hydrocarbons generally associated with crude commercial tetrachloroethylene also are subject to oxidative attack and decompose to some of the same products as those formed by the oxidation of tetrachloroethylene, and at a somewhat accelerated rate, as compared to the oxidation of tetrachloroethylene. These products are then available to catalyze the decomposition of the tetrachloroethylene. For example, tetrachloroethylene obtained commercially from the crude products of chlorination and chlorinolysis of lower aliphatic hydrocarbons may contain small but appreciable amounts of saturated and unsaturated chlorinated hydrocarbons, such as dichloroethylene, trichloroethylene, trichloroethane, unsymmetrical tetrachloroethane, pentachloroethane, and the like. These lower chloro-hydrocarbons in themselves are relatively innocuous in solvent extraction processes in which the tetrachloroethylene is used, but the oxidation decomposition products thereof corrode metal surfaces with which a body of tetrachloroethylene containing them comes into con-

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tact. These less stable chloro-hydrocarbons are believed to be the principal initial source of chloro-oxygen-containing impurities, such as phosgene, chloroacetic acid, trichloroacetic acid, and the like, in the tetrachloroethylene, which impurities catalyze decomposition of the tetrachloroethylene.

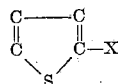
The problem, therefore, is principally one of inhibiting the initiation of the oxidation of the chlorohydrocarbons commonly associated with commercial tetrachloroethylene, as well as inhibiting the oxidation of tetrachloroethylene itself.

One of the objects of the present invention is to provide means for inhibiting oxidation of tetrachloroethylene and lower aliphatic chloro-hydrocarbons generally associated therewith during exposure to air, light, heat, moisture, and metal surfaces.

Another object of the invention is to provide a procedure for treating and purifying crude tetrachloroethylene in order to obtain maximum efficiency of the stabilizer in the purified product.

These and other objects will be apparent to those skilled in the art from the discussion hereinafter.

It has now been found that where the crude tetrachloroethylene, particularly that obtained from commercial processes involving the chlorinolysis of lower hydrocarbons or hydrocarbon chlorides, or the chlorination and simultaneous dehydrochlorination of hydrocarbon chlorides, such as ethylene dichloride, or of unsaturated hydrocarbons, such as acetylene, ethylene, ethane, and the like, contains appreciable amounts of lower chlorinated aliphatic hydrocarbons other than tetrachloroethylene as impurities, such crude product may initially be treated with an aqueous solution of an inorganic base and a high boiling point organic base in order to destroy the major portion of volatile acids and acid-forming impurities, and then combined with 2-chlorothiophene or 2-bromothiophene, whereby decomposition of the tetrachloroethylene and other lower chlorinated aliphatic hydrocarbons is inhibited under the most adverse conditions of storage and commercial use. In general, the present invention is directed to a composition stabilizing amounts of a compound of the general formula



wherein X is chlorine or bromine.

These compounds have been found particularly effective in stabilizing tetrachloroethylene contaminated with minor amounts of other lower aliphatic chloro-hydrocarbons, both in the liquid and in the vapor phase. For the most

part, the stabilizing effect has been found to be most pronounced and prolonged where pre-treatments which destroy the greater part of the chloro-acids and acid chlorides have been resorted to prior to combining the tetrachloroethylene with 2-chlorothiophene or 2-bromothiophene.

The initial treatment of the crude tetrachloroethylene may include adding an organic base of the amine type and having a boiling point higher than tetrachloroethylene, for example, aniline or morpholine, in an amount from approximately 0.2-2.0% by weight to the crude product, and fractionally distilling the crude mass to recover substantially all of the tetrachloroethylene as an intermediate fraction in the distillation; additional treatments may include washing the tetrachloroethylene fraction with a solution of an inorganic base, such as an alkali metal or alkaline earth metal base, for example, sodium hydroxide, sodium carbonate, calcium hydroxide, magnesium bicarbonate, and the like, drying the washed product and distilling the dried product to recover a more highly refined tetrachloroethylene fraction. The purpose in using an amine, such as aniline, is to allow for the reaction of such amine with acid chloride products contained in the crude product, whereby an anilide or analogous compound may form during distillation and the undesired impurity is retained in the distillation residue. The purpose of washing the effluent from the initial distillation with an alkali metal or alkaline earth metal base is to remove the more volatile of the acid chloride impurities, such as hydrogen chloride, phosgene, and the like, which may not have reacted with the amine.

The crude product may also be washed initially with a solution of an inorganic base, such as those noted above, dried, and combined with an amine having a boiling point substantially higher than tetrachloroethylene, generally in an amount from 0.2-2.0% by weight, and the mixture thus obtained distilled as described above in order to recover the purified tetrachloroethylene substantially free from chloro-oxygen-containing impurities.

Where such impurities as hydrogen chloride, phosgene, chloro-acids, and the like, are known to be extremely low in the crude product, this material may be combined with an amine, such as aniline, as noted hereinabove, and subjected to fractional distillation to recover the substantially pure tetrachloroethylene without the necessity of resorting to the treatment with a solution of an inorganic base. Moreover, the dilute alkaline wash may be omitted even where the chloro-oxygen-containing compounds are present in appreciable quantities in the crude product, but it has been found that the amount of organic amine consumed and the volume of distillation residue accumulated are excessive.

After any one of the above-described initial treatments, the recovered tetrachloroethylene may be combined with a stabilizing amount of 2-chlorothiophene or 2-bromothiophene, noted above, for example, in an amount from 0.01-1.0% by weight of tetrachloroethylene, preferably, however, from 0.2-0.3% where the above pre-treatments or their equivalent have been used. The extremes within the above-noted broad range are preferred where the amount of chloro-hydrocarbon impurities associated with the tetrachloroethylene is unusually high or unusually low, while the amounts within the in-

intermediate preferred range are generally sufficiently effective where the purified tetrachloroethylene contains not more than about 1-3% of the lower chlorinated aliphatic hydrocarbon impurities consisting essentially of trichloroethylene, the most common impurity obtained in commercial production.

The beneficial effects of the present invention may also be realized where tetrachloroethylene has been purified in a commercial operation and stabilized either with a high boiling point stabilizer, i. e., a stabilizer such as one of the amine or of the ether type having a higher boiling point than that of tetrachloroethylene, or with stabilizers which are more volatile than tetrachloroethylene, by removing such stabilizer as by chemical reaction, azeotropic distillation, or the like; the thus-treated mass is then fractionally distilled to recover the tetrachloroethylene fraction, which may be combined with a member of the group of 2-chlorothiophene and 2-bromothiophene, noted hereinabove, in an amount sufficient to effect stabilization, whereby the tetrachloroethylene is rendered especially suitable, due to its stability, for degreasing or dry cleaning operations.

In order that those skilled in the art may better understand the present invention and in what manner the same may be carried into effect, the following specific examples are offered:

#### Example I

Crude tetrachloroethylene obtained from the distillation unit of a commercial tetrachloroethylene plant is washed with a dilute solution of soda ash (10%), dried over anhydrous calcium chloride, and combined with 0.25% by weight of aniline, and the material subjected to fractional distillation. The fraction boiling between 120.5° and 121.5° C. is taken for a stability test. Two 25-ml. samples of the tetrachloroethylene are placed in round-bottom, one-neck flasks and to one of these samples there is added 0.25% by weight of 2-chlorothiophene. To each of the flasks there is added an amount of water equal to 2% by weight of the tetrachloroethylene and a weighed strip of aluminum foil; the contents of the flasks are subjected to reflux for a period of 24 hours. Thereafter, the tetrachloroethylene is extracted with distilled water, the extract analyzed for chloride ion (titration with 0.02N AgNO<sub>3</sub>) according to the Volhard method and the aluminum strips washed, dried and reweighed, with the following results:

Sample	Loss in Weight Al Strip	Gms. Cl/Liter Tetrachloroethylene
Containing 2-Chlorothiophene.	Less than 1 mg.	Trace.
Control.....	.....do.....	0.006.

#### Example II

A batch of crude chloro-hydrocarbons obtained from a commercial unit for the production of tetrachloroethylene and trichloroethylene is combined with 1% by weight of morpholine, whereupon a heavy white precipitate is formed. The mixture is subjected to reflux for a period of four hours and the crude mixture of chloro-hydrocarbons separated from the precipitate formed. The crude mixture is then subjected to fractional distillation and the fraction boiling

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from 120.2° C. to 121.7° C. is taken as the tetrachloroethylene cut. Two 25-ml. portions of this tetrachloroethylene cut are placed in round-bottom flasks and a strip of aluminum foil is added thereto. To one of the flasks is added 2-chlorothiophene in an amount of 0.25% by weight of the tetrachloroethylene contained therein, and to both of the flasks there is added 0.8 ml. of water. The flasks and contents are heated to the reflux temperature for tetrachloroethylene for a period of 24 hours, cooled, extracted with distilled water and the aluminum strips washed, dried and weighed, as in Example I, with the following results:

Sample	Loss in Weight Al Strip	Gms. Cl/Liter Tetrachloroethylene
Containing 2 - Chlorothiophene.	Less than 1 mg....	0.004
Control.....	do.....	0.010

#### Example III

A batch of crude chloro-hydrocarbons from a commercial unit producing tetrachloroethylene and trichloroethylene is initially treated to remove saturated chlorohydrocarbons and chloro-oxygen-containing compounds and subsequently fractionated to separate the tetrachloroethylene from the other chloro-hydrocarbons. Two 25-ml. portions of this tetrachloroethylene fraction are placed in round-bottom flasks and to one of the portions there is added 0.25% by weight of 2-chlorothiophene and to each of the flasks there is added 0.8 ml. of water and a weighed strip of aluminum foil. The contents of the flask are refluxed for a period of 24 hours, cooled, extracted with distilled water, and the strips of aluminum foil washed, dried and weighed, as in Example I, with the following results:

Sample	Loss in Weight Al Strip	Gms. Cl/Liter Tetrachloroethylene
Containing 2 - Chlorothiophene.	Less than 1 mg....	0.001
Control.....	do.....	0.049

#### Example IV

A crude mixture of chloro-hydrocarbons from a commercial unit for the production of tetrachloroethylene and trichloroethylene is combined with 1% by weight of aniline and subjected to fractional distillation. The tetrachloroethylene cut (B. P. 120.5-121.5° C.) is sampled when about one-half of the tetrachloroethylene has been recovered from the crude material, and again toward the end of the cut. The portion taken at the half-way point of the tetrachloroethylene cut is labeled "A" and that taken from the end of the tetrachloroethylene cut is labeled "B." 25-ml. portions of these two samples are subjected to the stability tests described in Example I above, with the following results:

Sample	Gain or Loss in Weight of Al Strip	Gms. Cl/Liter Tetrachloroethylene
Containing 2 - Chlorothiophene "A".	Less than 1 mg....	0.001
Control-"A".	do.....	0.009
Containing 2 - Chlorothiophene "B".	do.....	0.004
Control-"B".	do.....	0.007

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#### Example V

A crude mixture of chloro-hydrocarbons obtained from a commercial unit for the production of tetrachloroethylene or trichloroethylene is treated initially to remove saturated chloro-hydrocarbons and chloro-oxygen-containing compounds and subjected to fractional distillation, the following fractions being taken for stabilization tests:

Fraction No.	Boiling Point, °C.
1.....	119.1-121.4
2.....	121.6-121.9
3.....	121.9-122.0
4.....	122.0-130.0

Two 25-ml. portions of each of the above fractions are placed in round-bottom flasks and to one of these portions of each of the fractions there is added 0.25% by weight of 2-bromothiophene and to all of the portions there is added 0.8 ml. of water and a weighed aluminum strip. The flasks and contents are heated to the reflux temperature of tetrachloroethylene for a period of 24 hours and the tetrachloroethylene extracted with distilled water, as in Examples I-IV above, with the following results:

Sample	Loss in Weight of Al Strip	Gms. Cl/Liter Tetrachloroethylene
(1) 2-Bromothiophene.....	Less than 1 mg....	Trace.
Control.....	do.....	0.035
(2) 2-Bromothiophene.....	do.....	Trace.
Control.....	do.....	0.043
(3) 2-Bromothiophene.....	do.....	Trace.
Control.....	do.....	0.003
(4) 2-Bromothiophene.....	do.....	Trace.
Control.....	do.....	0.007

While there have been described various embodiments of the invention, the products described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A composition of matter consisting essentially of tetrachloroethylene and a stabilizing amount of a compound chosen from the group consisting of 2-chlorothiophene and 2-bromothiophene.

2. A composition of matter consisting essentially of tetrachloroethylene and a stabilizing amount of 2-chlorothiophene.

3. A composition of matter consisting essentially of tetrachloroethylene and a stabilizing amount of 2-bromothiophene.

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The following references are of record in the file of this patent:

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