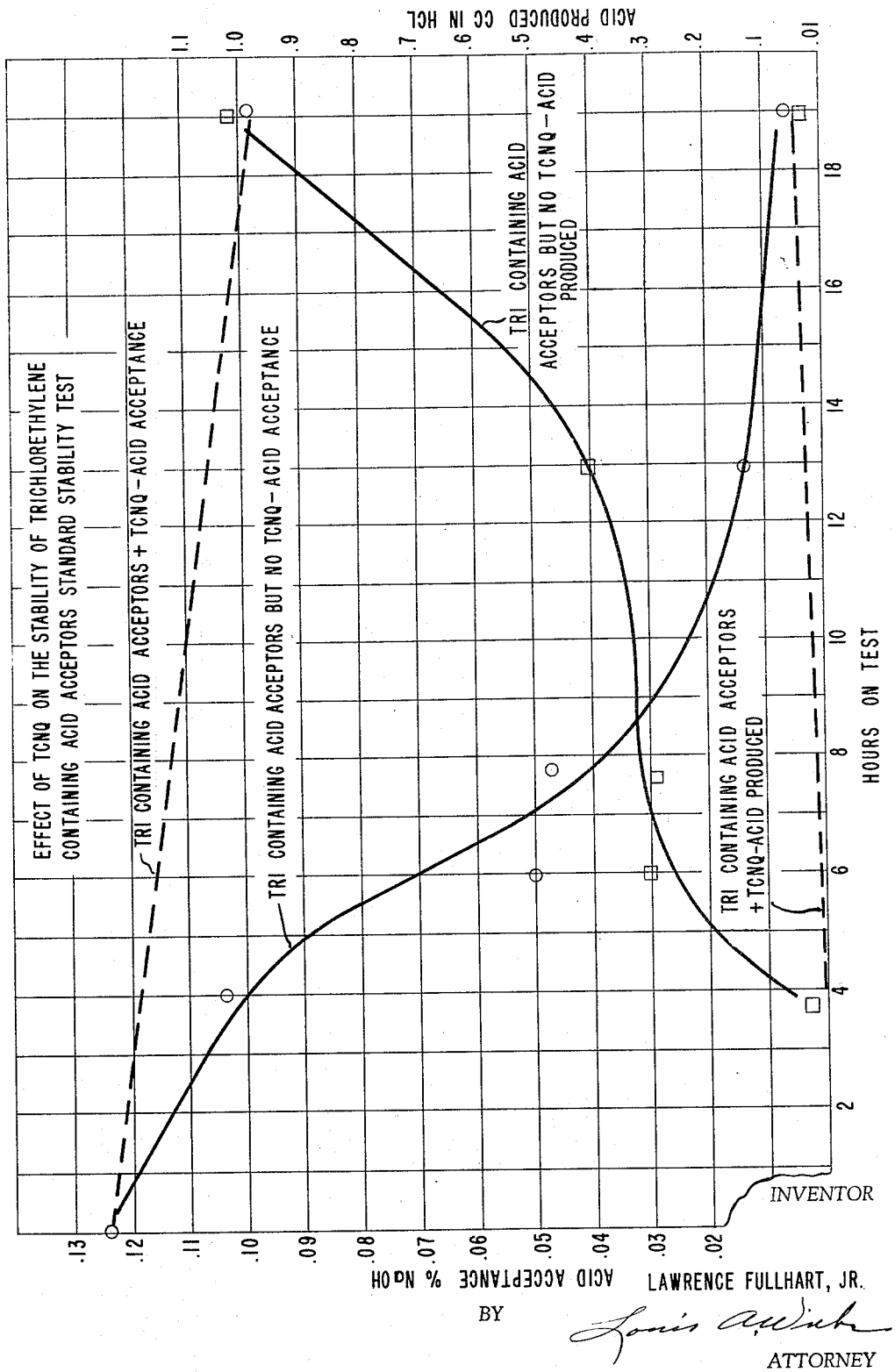
Oct. 4, 1966 L. FULLHART, JR 3,277,193

CHLORINATED HYDROCARBONS STABILIZED
WITH CERTAIN POLYCYANO COMPOUNDS
Filed June 28, 1962



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United States Patent Office 3,277,193 Patented Oct. 4, 1966

3,277,193

CHLORINATED HYDROCARBONS STABILIZED WITH CERTAIN POLYCYANO COMPOUNDS

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Filed June 28, 1962, Ser. No. 206,056
2 Claims. (Cl. 260—652.5)

This invention relates to chlorinated hydrocarbons, and more particularly it relates to new and improved chlorinated hydrocarbons containing therein agents to promote the stability thereof.

Chlorinated hydrocarbons, particularly trichlorethylene, perchlorethylene, methyl chloroform and the like have long been used commercially as cleaning and degreasing compounds. It is well known that in the presence of air, oils, greases, metals and other substances present in cleaning and degreasing operations, chlorinated hydrocarbons break down yielding products such as hydrogen chloride which when present even in small quantities causes serious corrosion problems. These problems are particularly severe in the degreasing or cleaning of aluminum.

It is apparent that the decomposition of chlorinated hydrocarbons is sometimes initiated by the formation therein of free radicals, for example, hydrogen free radicals (H·) or possibly other free radicals such as methyl chloride free radicals (CH_2Cl·), ethyl chloride free radicals (C_2H_4Cl·) or the like. The presence of such free radicals may be caused by ultraviolet light or by the presence of free radical initiating compounds. The free radicals are very reactive to catalyze the decomposition of chlorinated hydrocarbons to form HCl and possibly other acids therein.

Heretofore, small quantities of stabilizing agents have been added to chlorinated hydrocarbons to stabilize the same against deterioration by oxidation or heat or by acid acceptance of acids formed therein. Acid acceptors by acceptance of the formed acids soon become exhausted and an objectionable concentration of acid builds up in the chlorinated hydrocarbons.

It is an object of this invention to stabilize chlorinated hydrocarbons against the formation therein of an objectionable concentration of acids.

It is another object to eliminate or render innocuous free radicals that may be present in a chlorinated hydrocarbon.

It is an object of this invention to provide a new and improved chlorinated hydrocarbon solvent.

It is still another object of this invention to provide a chlorinated hydrocarbon composition that will be operative as a degreasing or cleaning solvent for longer periods of time without objectionable acid build up.

Other objects will appear hereinafter.

It has now been found, in accordance with this invention, that the presence in a chlorinated hydrocarbon solvent, such as trichlorethylene, perchlorethylene, methyl chloroform or the like, of a small amount of a cyano compound taken from the group consisting of tetracyanoquinodimethane, tetracyanoethylene, 1,2-dicyano-1,2-bis(trifluoromethyl) ethylene and tetracyanodithiin will greatly reduce the amount of HCl formed in a chlorinated hydrocarbon under given conditions similating commercial operation.

This reduction of acid formation under given conditions will be obtained when one of the aforesaid cyano compounds is present in otherwise unstabilized trichlorethylene or when present in trichlorethylene containing other well-known stabilizers.

In order to simplify the description of this invention specific reference will hereinafter be made to trichlorethylene as a representative chlorinated hydrocarbon, it being understood that other liquid chlorinated hydrocarbon solvents such as perchlorethylene, methyl chloroform and the like will be stabilized to a comparable extent.

Inasmuch as the aforesaid cyano compounds are relatively new compounds, the following references are given for a description as to how these compounds are obtainable.

Tetracyanoethylene, hereinafter referred to as TCNE, is described in an article by Cairns et al. in JACS vol. 80, p. 2775 (1958).

Tetracyanoquinodimethane, hereinafter referred to as TCNQ, is described in an article by Acker et al. JACS vol. 82, p. 6408 (1960).

Tetracyanodithiin, hereinafter referred to as TCS2, is described in U.S. Patent No. 3,008,967 issued in the names of Blomstrom and Smith.

1,2-dicyano-1,2-bis(trifluoromethyl) ethylene, hereinafter referred to as DCFE is described in U.S. patent application S.N. 71,390, filed November 25, 1960, now U.S. Patent No. 3,113,115.

The stabilization of chlorinated hydrocarbons against excessive acid formation will be obtained by the presence in the chlorinated hydrocarbon of about 0.001% to about 0.1% by weight of a cyano compound taken from the group consisting of TCNE, TCNQ, TCS2 and DCFE. Less than about 0.001% of the cyano compound would not sufficiently effect the stabilization, and the inclusion of greater than 0.1% would not be warranted by reason of expense.

The effectiveness of the stabilization of a chlorinated hydrocarbon by the presence of the cyano compounds in accordance with this invention is illustrated by the following examples in which the degree of stabilization is given in terms of acid produced (cc. of 1 N HCl) and acid acceptance as percent of NaOH.

By the term "acid produced (cc. of 1 N HCl)" is meant the total amount of acid produced by the test conditions as determined by titrating the resulting composition with standard sodium hydroxide solution.

By the term "acid acceptance as percent of NaOH" is meant the acid acceptance, as weight percent of NaOH, determined in the following manner:

(1) Prepare a methanol-CHl solution by adding 1.5 ml. concentrated (37%) reagent grade HCl to 400 ml. absolute reagent grade methanol.

To 25 ml. of this solution, add 25 ml. distilled water. Then add 4–5 drops of phenolphthalein and titrate with standard NaOH to pink endpoint, i.e., to the first pink color which lasts at least 15 sec. Let the titer be R ml.

(2) Pipette a 15 ml. sample of the chlorinated hydrocarbon in question into a 250 ml. flask and add 25 ml. of the titrated methanol-HCl solution as prepared under paragraph 1 above.

(3) Reflux the mixture for 5 minutes.

(4) Cool the refluxed mixture and add 25 ml. of neutral distilled water.

(5) Add 4–5 drops of phenolphthalein indicator and titrate with standard NaOH to pink endpoint. Let the titer be S ml.

Now subtract the titer of the refluxed sample mixture, S, from that of the reagent, R, to find the ml. of HCl accepted by the sample. The latter value is converted into "acid acceptance" by the following equation:

$$\frac{(R-S)\times N\times 0.04}{15\times 1.463}\times 100 = \text{acid acceptance (Calc'd as percent NaOH)}$$

where N is the normality of the standard NaOH solution (the density of trichlorethylene is about 1.463). For N=0.1; (R—S) (0.0182)=percent NaOH.

Example 1

The following 16 hour standard stability test was carried out with two trichlorethylene compositions containing a combination of well-known trichlorethylene stabilizers but only one of which contained one of the cyano compounds of this invention, namely DCFE.

In this test 200 ml. of the trichlorethylene to be tested was refluxed for a period of 16 hours. The distillate was allowed to return to the flask through a 50 ml. water trap. To the solution was added 0.1 gram powdered iron, and oxygen was bubbled in at a rate of about 20 ml. per min. The boiling solution was placed in close proximity to a source of ultraviolet light. The stability of the solution was determined by titrating both the water solution from the trap and the solvent with standard sodium hydroxide solution to measure the total amount of acid produced, and the acid acceptance was calculated as set forth above.

Ex. No.	Solvent	Acid Produced, cc. of 1 N HCl	A.A. as Percent NaOH	A.A., Percent Remaining
1	Trichlorethylene stablized with .02% N-methylpyrrole, 25 p.p.m. triethyl amine, .4% of butylene oxide and epi-chlorohydrin.	1.58	.007	4
2	Same as above plus .01% DCFE.	0.31	.068	53

A.A.=acid acceptance.

Example 1 containing one of the best previously known combinations of trichlorethylene stabilizers, after 16 hours reflux retained only 4% of the acid acceptance originally present in the trichlorethylene. Example 2 shows that trichlorethylene stabilized with the same combination of stabilizers but also containing 0.01% of DCFE under the same conditions retained 53% of the acid acceptance originally present.

In the following examples the same stability test was conducted for a period of four hours with the following results:

Ex. No.	Solvent	Cc. of 1 N HCl Produced
3	Trichlorethylene (control)	1.73
4	Trichlorethylene plus .005% TCNQ	0.15
5	Trichlorethylene plus .005% TCNE	0.62
6	Trichlorethylene plus (.2% diisobutylene, .01% pentaphen).	1.38
7	Trichlorethylene plus (.2% diisobutylene, .01% pentaphen) plus .005% TCNQ.	0.38
8	Trichlorethylene plus (.2% diisobutylene, .01% pentaphen) plus .005% TCNE.	0.55
9	Trichlorethylene plus (.2% diisobutylene, .01% pentaphen) plus .01% DCFE.	0.46
10	Trichlorethylene plus (.4% butyleneoxide, .2% ethyl acetate, .05% diisobutylene, 25 p.p.m. triethylamine).	1.0
11	Trichlorethylene plus (.4% butyleneoxide, .2% ethyl acetate, .05% diisobutylene, 25 p.p.m. triethylamine) plus .005% TCNQ.	0.02
12	Methyl chloroform	1.36
13	Methyl chloroform plus .005% TCNQ	0.30

Trichlorethylene is often fortified with so-called acid acceptors, for example, certain epoxides, as well as other stabilizers against the action of oxidation and heat. These acid acceptors are compounds which react with the acid formed during decomposition. By reacting with the acid produced they prevent the solution from becoming acid. Thus, it is possible to measure the value of a stabilizer by determining its effect on the acid acceptors.

The accompanying diagram, the sole figure, illustrates the decrease in acid acceptance of trichlorethylene stabilized with: .02% n-methyl pyrrole, 25 p.p.m. triethyl amine and .4% butylene oxide and epi-chlorohydrin during a 19 hour standard stability test and how the addition of TCNQ greatly increases the stability of the trichlorethylene and the high acid acceptance remaining after 19 hours of the test. The test was carried out in the same way as the above-defined standard stability tests.

The standard stability test data on which the diagram, the sole figure, is based is shown below in Table I.

TABLE I

[Standard stability test data showing that trichlorethylene partially stabilized loses acid acceptance whereas, with TCNQ added the solution remains stable]

Test Solution	Time in Hrs.	Cc. of 1N HCl Produced	A.A. as Percent NaOH	Percent A.A. Remaining
Trichlorethylene*	0	0	0.125	100
Do	4	.032	0.105	84
Do	6	.306	0.051	41
Do	7.5	.296	0.048	38
Do	13	.42	0.014	11
Do	19	1.03	0.007	6
Trichlorethylene* plus .005% TCNQ	19	0.4	0 100	80

* The trichlorethylene also contained the following stabilizers: .02% N-methyl pyrrole, 25 p.p.m. triethylamine, .4% butylene oxide and epi-chlorohydrin.

The following examples disclose the results in percent of acid acceptance remaining (based on 100% acid acceptance at start of test) after a sixteen hour standard stability test on trichlorethylene containing .02% N-methyl pyrrole, 25 p.p.m. triethylamine and .4% butylene oxide and epi-chlorohydrin, with and without certain of the cyano compounds added in accordance with this invention.

Example No.	Solvent	Percent A. A. Remaining
14	Trichlorethylene	5.6
15	Trichlorethylene plus .005% TCNQ	80.0
16	Trichlorethylene plus .015% DCFE	57.0
17	Trichlorethylene plus .01% TCS2	70.0

Example 18

The following 16 hour standard stability test was carried out with two perchlorethylene compositions only one of which contained one of the cyano compounds of this invention, namely DCFE.

In this test 200 ml. of perchlorethylene was refluxed for a period of 16 hours. The distillate was allowed to return to the flask through a 50 ml. water trap. To the solution was added 0.1 gram powdered iron, and oxygen was bubbled in at a rate of about 20 ml. per minute. The boiling solution was placed in close proximity to a source of ultraviolet light. The stability of the solution was determined by titrating both the water solution from the trap and the solvent with standard sodium hydroxide solution to measure the total amount of acid produced.

The sample of perchlorethylene in which nothing was added, after the 16 hour test, contained 9.7 cc. of 1 N HCl. The sample in which the perchlorethylene contained 0.1% DCFE had an acid content of 4.9 cc. of 1 N HCl.

Throughout the specification and claims, any reference to parts, proportions and percentages refers to parts, proportions and precentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

I claim:

1. A chlorinated hydrocarbon taken from the group consisting of trichlorethylene, perchlorethylene and

methyl chloroform, said chlorinated hydrocarbon containing .001% to .1% by weight of a cyano compound taken from the group consisting of tetracyanoethylene, tetracyanoquinodimethane, tetracyanodithiin and 1,2-dicyano-1,2-bis(trifluoromethyl) ethylene.

2. Trichlorethylene containing .001% to .1% by weight of a cyano compound taken from the group consisting of tetracyanoethylene, tetracyanoquinodimethane, tetracyanodithiin and 1,2-dicyano-1,2-bis(trifluoromethyl) ethylene.

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