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STABILIZATION OF TRICHLORETHYLENE

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This invention relates to a stabilized degreasing composition and a method of stabilizing trichlorethylene for use in degreasing all kinds of metals and alloys including those metals and their alloys which by themselves or through their salts, particularly their anhydrous chlorides, exhibit a specific decomposing effect on trichlorethylene.

Trichlorethylene is known to be subject to decomposition by oxygen of the air, and this decomposition is accelerated by heat and light. Therefore trichlorethylene which is to be used in degreasing metals is normally stabilized against such oxidation by a number of classes of chemical additives known to the art. However, trichlorethylene so stabilized is not completely satisfactory and is considered not to be fully stabilized for degreasing all kinds of metals and metal alloys. In the first place, certain of these chemical additives undergo reactions involving the additive, the trichlorethylene and certain metals being degreased, and these reactions are undesirable, particularly in providing a stabilized trichlorethylene for use in the degreasing of metals. Among the antioxidants showing this tendency are the amines. In the second place certain metals and alloys and/or their salts, particularly the anhydrous chlorides such as aluminum and/or its chloride and perhaps iron and certain other metals and salts, exhibit a specific decomposing effect on trichlorethylene which effect and its attendant difficulties in degreasing is well known and has been frequently described in the art. Against this decomposing effect the usual antioxidants are ineffective or are present in quantities too small to exert any practical retarding or inhibiting influence.

Thus unless trichlorethylene is further stabilized to prevent the additional problems cited above it is not completely satisfactory for degreasing of metals.

For the inhibition of the decomposing effect of aluminum and perhaps certain other metals and/or their salts, aliphatic alcohols and other oxygen compounds have been proposed as set forth, for example, in U.S. Patent No. 2,371,644. The most effective of these are the primary aliphatic alcohols, the secondary and tertiary alcohols being less effective. Esters and ethers also are much less effective. However, experience has shown that primary alcohols in trichlorethylene as inhibitors against the metal induced decomposition produce corrosion problems. For instance, under anhydrous conditions, trichlorethylene containing them is extremely corrosive to magnesium metal and its alloys, and in the presence of moisture, trichlorethylene containing these primary alcohols is corrosive to ferrous metals and alloys. Because this corrosion of metals by trichlorethylene containing the primary alcohols presents a serious problem, use of these in the art of inhibiting trichlorethylene against this metal induced decomposition was discontinued, and since the other oxygen containing compounds were less effective they were not considered to provide a satisfactory answer to the problem.

Recently a method of inhibiting against this metal induced decomposition was proposed which combines the use of esters and ethers. However, like the primary aliphatic alcohols, trichlorethylene containing this combination is corrosive to ferrous metals in the presence of moisture.

A primary object of the present invention is the provision of a method of stabilizing trichlorethylene against metal induced decomposition, while at the same time providing a stabilized trichlorethylene which is substantially non-corrosive to ferrous metals and to the light metals.

A further object of the invention is the provision of trichlorethylene which is stabilized against metal influenced decomposition and at the same time is non-corrosive to metals.

A still further object of the present invention is the provision of a method of preventing metal induced decomposition of trichlorethylene in the degreasing of light metals.

The objects set forth above are achieved in the practice of the present invention by adding to the trichlorethylene relatively small amounts of a synergistically cooperative pair of additives consisting of (a) secondary or tertiary aliphatic monohydric alcohols and (b) epoxides. Such secondary or tertiary alcohols used alone are not satisfactory or effective in preventing metal induced decomposition of trichlorethylene, particularly where such solvent is used in the degreasing of light metals. The same is true as to the use of epoxides alone. However, I have discovered that when used in combination as a cooperative pair the effectiveness of each additive, and hence the total effectiveness of the combination, is substantially increased, as will be apparent from a study of the examples set forth below. It has further been discovered that trichlorethylene containing these secondary or tertiary alcohols is essentially non-corrosive toward magnesium, which is completely unlike the effect of unlike primary aliphatic alcohols, and it has further been discovered that trichlorethylene containing these synergistically cooperative pairs of secondary or tertiary alcohols and expoxides is essentially non-corrosive toward ferrous metals in the presence of moisture and is significantly less corrosive toward ferrous metals in the presence of moisture than previous compositions known to the art. These facts are likewise apparent from a study of the examples set forth below.

The metal induced decomposition referred to above takes place when certain metals are degreased whose anhydrous halides are active metal salts which are capable of inducing certain condensation reactions, and perhaps other types of reactions, with trichlorethylene or with other chlor hydrocarbons which may be present in trichlorethylene. When such reactions take place there can develop a rapid decomposition of the trichlorethylene. It is believed that an active metal halide such as aluminum chloride in its anhydrous condition is the active catalyst or agent bringing about such metal induced or metal catalyzed decomposition. One of the results of the metal induced or active chloride catalyzed decomposition reaction is the production of color bodies which greatly reduce the transmission of light through the trichlorethylene thus affected. This fact has made it possible to devise a laboratory test for evaluating materials added to trichlorethylene as inhibitors or stabilizers. This test is carried out by determining the amount of visible light transmission through the trichlorethylene after exposure to an active metal chloride such as aluminum chloride. The degree of decomposition of the solvent, or, conversely, the degree of inhibition of decomposition, is indicated by the relative amount of such visible light transmission. This light transmission test is carried out as follows:

Trichlorethylene (50 ml. commercial grade) containing no inhibitors against active chloride catalyzed decomposition is refluxed for 15 minutes. In order to insure the absence of water, the solvent is boiled rapidly without a condenser and the vapors allowed to escape into a hood

for 10 seconds, after which the flask and contents are rapidly cooled and about 0.3 gm. of fresh anhydrous $AlCl_3$ added to the solvent. This solvent containing the $AlCl_3$ is refluxed for 15 minutes after which it is cooled, and the suspended, inactivated aluminum chloride separated from the solvent by settling and decantation, or by centrifugation for about 1 minute at 1500 r.p.m. The light transmission through a series of related gelatin filters covering the visible light spectrum is determined in a Cenco (Central Scientific Company) Photolometer (a colorimeter or electrophotometer) using untreated trichlorethylene as the standard and setting the transmission through this untreated trichlorethylene at 100% transmission for each of the four filters. This visible light transmission test was applied in carrying out the following examples:

Example 1.—Seconadry propyl alcohol-butylene oxide

50 ml. of commercial trichlorethylene containing no inhibitor was freed from water by boiling in a flask without a condenser and allowing the vapors to escape for 10 seconds. Immediately the flask and contents were cooled and about 0.3 grams of anhydrous $AlCl_3$ was added. The solvent was then refluxed for 15 minutes. Then the flask and contents were cooled and the suspended matter separated. The visible light transmission through the solvent was measured with a Cenco Photolometer. The transmission was 0.0.

Commercial trichlorethylene inhibited with varying percentages of isopropyl alcohol (secondary propyl alcohol) and varying percentages of butylene oxide and combinations of these two whose total percentage concentrations equalled one or more of the concentrations of either additive alone, was treated as in the procedure outlined above with results shown below:

Alcohol	Percent conc.	Epoxide	Percent conc.	Percent light transmission
Isopropyl	.06	0.0	0.0	35.02
0.0	0.0	Butylene oxide	.06	4.5
Isopropyl	.03	do	.03	84.5
Do	.12	0.0	0.0	67.9
0.0	0.0	Butylene oxide	.12	69.0
Isopropyl	.06	do	.06	95.2

Example 2.—Secondary butyl alcohol-epichlorhydrin

Another series in which secondary butyl alcohol and epichlorhydrin were used both alone and as a cooperative pair was similarly tested with these results:

Alcohol	Percent conc.	Epoxide	Percent conc.	Percent light transmission
Sec. butyl	.06	0.0	0.0	84.4
0.0	0.0	Epichlorhydrin	.06	86.6
Sec. butyl alc	.03	do	.03	94.0
Sec. butyl	.12	0.0		[1] 39.9
0.0	0.0	Epichlorphydirn	.12	[1] 18.4
Sec. butyl	.06	do	.06	[1] 69.4

[1] Approximately 0.4 gm. $AlCl_3$ used.

Example 3.—Tertiary butyl alcohol-butylene oxide

A similar series of tests was performed with tertiary butyl alcohol and butylene oxide with the following results:

Alcohol	Percent conc.	Epoxide	Percent conc.	Percent light transmission
Tert.-butyl	.06	0.0	0.0	33.8
0.0	0.0	Butylene oxide	.06	4.5
Tert.-butyl	.03	do	.03	50.8
Do	.12	0.0	0.0	53.1
0.0	0.0	Butylene oxide	.12	69.0
Tert.-butyl	.06	do	.06	98.17

Example 4.—Secondary amyl alcohol-2-pentene oxide

A fourth series of tests similar to those outlined in Example 1 were performed in which secondary amyl alcohol and 2-pentene oxide were the alcohol-epoxide cooperative pair. The following results were obtained:

Alcohol	Percent conc.	Epoxide	Percent conc.	Percent light transmission
Sec. amyl	.06	0.0	0.0	23.5
0.0	0.0	2-pentene oxide	.06	14.4
Sec. amyl	.03	do	.03	48.7
Do	.12	0.0		55.9
0.0	0.0	2-pentene oxide	.12	66.0
Sec. amyl	.06	do	.06	79.0

The alcohols of the present invention consist of secondary propyl, secondary butyl and secondary amyl alcohols and tertiary butyl and tertiary amyl alcohols. Included among the secondary amyl alcohols are methyl propyl carbinol, methyl isopropyl carbinol and diethyl carbinol. The epoxides of the present invention comprise the following:

Cyclohexene oxide
Ethyl glycidyl ether
Allyl glycidyl ether
Isopropyl glycidyl ether
Diisobutylene oxide
Epichlorhydrin
Butylene oxide
2-pentene oxide

All of the above alcohols and epoxides have been tested and found to be synergistically cooperative as in the examples given.

In order to insure the proper distribution of these cooperative pairs throughout a degreasing system as well as proper distribution of any other additives used, it has been found advantageous to use at least two of any one additive, the two additives having boiling points above and below the boiling point of the trichlorethylene. For example, in a synergistically cooperative pair of secondary alcohol and epoxide we may choose to use a pair of alcohols and a pair of epoxides as follows:

Example 5

Trichlorethylene plus:
Isopropyl alcohol
Butylene oxide
Sec. butyl alcohol
Epichlorhydrin

Example 6

Trichlorethylene plus:
Isopropyl alcohol
Butylene oxide
Sec. amyl alcohol
Ethyl glycidyl ether

Example 7

Trichlorethylene plus:
Isopropyl alcohol
Butylene oxide
Methyl propyl carbinol
Diisobutylene oxide

It is also advantageous in the practice of the present invention to use three secondary or tertiary alcohols and three epoxy compounds with boiling points selected so that there will be one alcohol and one epoxide having boiling points above the boiling point of trichlorethylene, one alcohol and one epoxide having boiling points substantially at the boiling point of trichlorethylene and one alcohol and one epoxide having boiling points below the

boiling point of trichlorethylene. An example of this embodiment of the present invention is as follows:

Example 8

Trichlorethylene plus:
- Isopropyl alcohol
- Butylene oxide
- Tertiary amyl alcohol
- 2-pentene oxide
- Sec. amyl alcohol
- Epichlorhydrin

Trichlorethylene stabilized with the synergistically cooperative pairs of the present invention is substantially non-corrosive to the light metals and to ferrous metals as shown in the following test results.

The test procedure used in determining the degree of corrosiveness was as follows:

150 ml. of tri (trichlorethylene) in a flask with 1%–2% (by vol.) water added and a polished weighed strip of cold rolled steel, cut to such dimensions that half the metal is in the liquid phase and half in the vapor phase, are heated to just below the boiling point and kept at this temperature for 96 or 112 hours. This test allows dissolved air to remain in the solvent which in the presence of water can cause corrosion of the steel and this corrosion can be greatly accelerated by the solvent or additives therein.

Using this procedure the following results were obtained:

	Solvent	Water present, percent	Hours	Metal	Loss, mgms.
A	Commercial tri A qualitatively found to contain: N-Me pyrrole, Epichlorhydrin, Isopropyl acetate, Trace of diisopropylamine	1	96	Steel	147.1
B	Commercial tri B qualitatively found to contain: N-Me pyrrole, Butylene oxide, Ethyl acetate, Trace of diisopropylamine	1	96	do	134.5
C	Trichlorethylene: Diisopropylamine, .009% wt, N-Me pyrrole, .02% wt, Epichlorhydrin, .12% wt, Sec. butyl alcohol, .12% wt	1	112	do	7.4
D	Trichlorethylene: N-Me pyrrole, .02% wt, Isopropanol, .15% wt, Sec. butanol, .15% wt, Butylene oxide, .12% wt, Epichlorhydrin, .12% wt, Diisopropylamine, .009% wt	1	96	do	2.5

In addition to the above results the non-corrosive nature of secondary and tertiary alcohols in trichlorethylene toward magnesium (a light metal which is very easily attacked by primary alcohols in trichlorethylene) was indicated by total reflux tests on solvent-alcohol compositions without added water as shown by the following results which include two examples in which primary alcohols were used:

	Solvent used	Time of test, days	Added water	Metal	Loss, mgms.
1	Tri only	13	None	Magnesium	0.9
2	Tri plus 0.4% (vol.) isobutanol	3	do	do	310.2
3	Tri plus 0.4% (vol.) sec. butanol	10	do	do	6.4
4	Tri plus 0.4% (vol.) tert. butanol	10	do	do	0.1
5	Tri plus 0.4% (vol.) n-propanol	7	do	do	153.2
6	Tri plus 0.4% (vol.) isopropanol	7	do	do	1.4
7	Tri plus 0.4% (vol.) cyclohexanol (a sec. alcohol).	7	do	do	1.0

In carrying out the present invention, the quantity of epoxide added should preferably be about the same in amount by weight as the amount of secondary or tertiary alcohol. However, alcohol-epoxide ratios of between about 1 to 10 and 10 to 1 may be employed with good results. The weight of each component of the synergistic pair of additives should be between about 0.01% and 1% of the weight of the trichlorethylene. A preferred combination of such synergistic additives consists of about 0.30% by weight secondary or tertiary alcohol and about 0.24% by weight epoxide. In the case of the embodiment of the present invention represented by the use of two pairs of synergistically cooperative additives as exemplified by Examples 5 to 7 inclusive, the preferred amount of each secondary or tertiary alcohol is 0.15% and the preferred amount of each epoxide is 0.12%. Likewise, in the embodiment involving the use of three alcohols and three epoxides as exemplified by Example 8, the preferred amount of each alcohol is 0.10% and of each epoxide is 0.08%. The alcohols of the present invention consist of the secondary and tertiary aliphatic monohydric alcohols having from 3 to 5 carbon atoms. The primary alcohols are specifically excluded. The epoxides of the present invention have from 3 to 8 carbon atoms.

Having thus described my invention, I claim:

1. A composition of matter consisting essentially of stabilized trichlorethylene containing synergistically cooperative additive consisting of (1) a monohydric alcohol selected from the group consisting of unsubstituted secondary and tertiary aliphatic monohydric alcohols having from 3 to 5 carbon atoms, and (2) an epoxide selected from the group consisting of epichlorhydrin, butylene oxide, diisobutylene oxide, isopropyl glycidyl ether, ethyl glycidyl ether, allyl glycidyl ether, 2-pentene oxide and cyclohexene oxide, each of said additives being present in amounts between about 0.01% and 1% of the weight of the trichlorethylene.

2. The composition of claim **1** in which the alcohol is isopropyl alcohol and the epoxide is butylene oxide.

3. The composition of claim **1** in which the alcohol is secondary butyl alcohol and the epoxide is epichlorhydrin.

4. The composition of claim **1** in which the alcohol is tertiary butyl alcohol and the epoxide is butylene oxide.

5. The composition of claim 1 in which the alcohol is secondary amyl alcohol and the epoxide is 2-pentene oxide.

6. A composition of matter consisting essentially of stabilized trichlorethylene containing synergistically cooperative additives consisting of (1) two monohydric alcohols selected from the group consisting of unsubstituted secondary and tertiary aliphatic monohydric alcohols having from 3 to 5 carbon atoms, one of which has a boiling point above that of trichlorethylene and the other of which has a boiling point below that of trichlorethylene, and (2) two epoxides selected from the group consisting of epichlorhydrin, butylene oxide, diisobutylene oxide, isopropyl glycidyl ether, ethyl glycidyl ether, allyl glycidyl ether, 2-pentene oxide and cyclohexene oxide, one of which has a boiling point above that of trichlorethylene and the other of which has a boiling point below that of trichlorethylene, each of said additives being present in amounts between about 0.01% and 1% of the weight of the trichlorethylene.

7. A composition of matter consisting essentially of stabilized trichlorethylene containing synergistically cooperative additives consisting of (1) three monohydric alcohols selected from the group consisting of unsubstituted secondary and teritiary aliphatic monohydric alcohols having from 3 to 5 carbon atoms, one of which has a boiling point above that of trichlorethylene, one of which has a boiling point substantially the same as that of trichlorethylene and one of which has a boiling point below that of trichlorethylene, and (2) three epoxides selected from the group consisting of epichlorhydrin, butylene oxide, diisobutylene oxide, isopropyl glycidyl ether, ethyl glycidyl ether, allyl glycidyl ether, 2-pentene oxide and cyclohexene oxide, one of which has a boiling point above that of trichlorethylene, one of which has a boiling point substantially the same as that of trichlorethylene and one of which has a boiling point below that of trichlorethylene, each of said additives being present in amounts between about 0.01% and 1% of the weight of the trichlorethylene.

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