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METHOD OF STABILIZING TRICHLOROETHYLENE AND STABILIZING COMPOSITION THEREFOR

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The present invention relates to a method of stabilizing trichloroethylene and to a stabilizing composition therefor.

It is known that trichloroethylene is utilized industrially in various technical processes, particularly as a solvent for degreasing metals. Since trichloroethylene is an unstable chemical compound, the solvent is easily decomposed during such processes. The phenomena of decomposition of trichloroethylene are enhanced by the presence of air, light, moisture and heat, particularly when the solvent is in contact with metallic surfaces, such as iron and aluminum. As these phenomena are of an autocatalytic nature, it is most important to effectively stabilize the solvent, especially in view of the fact that the hydrochloric acid formed by the decomposition of trichloroethylene develops for example in steel or aluminum articles, which are being degreased, the chloride of these metals, which chlorides, in turn, enhance very much the decomposition process of the solvent under formation of more hydrochloric acid and subsequent strong corrosion of the metallic articles being degreased.

It is known in the art to use various types of organic substances for stabilizing trichloroethylene, such as the amines, phenols, alcohols, epoxides and esters; these substances are used as stabilizers either individually or in synergetic combinations. The most modern systems of stabilizing trichloroethylene are, in fact, based on the admixture of synergetic combinations of various compounds to trichloroethylene, such as, for instance, epoxides + amines

It is the object of our present invention to provide an improved method and composition for stabilizing trichloroethylene which is particularly suited to prevent decomposition of the latter when used in processes for degreasing metals.

It is another object of our invention to improve the conditions of working with trichloroethylene as a solvent by providing a method and stabilizing composition which suppress the accumulation of acid products in trichloroethylene or neutralizes the same when formed.

The objects of our invention are attained with the aid of our technically improved method of stabilizing trichloroethylene which makes use of a heretofore unknown synergetic mixture.

Our invention is based on the discovery that it is possible to produce a synergetic action of stabilizing trichloroethylene when a quaternary combination is added to trichloroethylene, the mixture containing a hydrazine derivative, an epoxide, an alcohol and a phenolic compound.

The hydrazine derivative may be one of the group comprising N,N-dimethylhydrazine, benzalazine, diethyl-

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ideneazine, and dimethylketazine, and is admixed to trichloroethylene in amounts of from 0.01% to 0.02% by weight approximately.

The epoxide may be, for instance, one of the group comprising butylene oxide, propylene oxide, amylene oxide, or chloropropylene oxide and is added to trichloroethylene in amounts of from 0.2% to 0.3% by weight approximately.

The alcohol may be one of the group comprising isobutyl alcohol, butyl alcohol, propyl alcohol, isopropyl alcohol, amyl alcohol, isoamyl alcohol, ethyl alcohol, and may be added to trichloroethylene in amounts of from 0.05% to 0.1% by weight approximately.

The phenolic compound may be chosen from the group comprising phenol, thymol, ortho-nitrophenol, eugenol, isopropyl-p-hydroxyanisole, ethyl-p-hydroxyanisole, and should be added to trichloroethylene preferably in quantities of from 0.005% to 0.01% by weight approximately.

The quantities of the components of the synergetic mixture may be chosen larger or smaller than the amounts given above depending upon the stabilizing effects to be attained and according to the other adjuvants which may be present in the solvent.

Such adjuvants are mentioned in our copending application Serial No. 747,566, filed July 18, 1958, now abandoned, and may be for instance, esters or alcohols and the like compounds which may be added to the trichloroethylene degreasing solvent without affecting intrinsically or substantially the synergetic effect of the quaternary mixture of the present invention.

The synergetic mixture according to the invention may contain one or several substances for each type of the components mentioned further above, and chosen from the list of substances mentioned for each type. For example, the group of the phenols may be represented in the synergetic mixture not only by phenol itself, but may also consist of a mixture of phenol and thymol; as representative of the class of epoxides, a mixture of propylene oxide and butylene oxide may be added, and the same applies to the other two groups, to be present as components in the synergetic mixture.

The technical advantages achieved with the present invention are illustrated by the following test series in which samples of trichloroethylene, stabilized by various methods, are classified according to their stability properties as revealed on the basis of a 48-hour accelerated oxidation test as specified in U.S.A. Army-Navy-Aeronautical Specification MIL-T7003 and Federal Specification OT-63a/.

This stability test consists essentially in causing 200 ml. of trichloroethylene to boil for 48 hours in a Pyrex flask of 500 ml. with reflux condenser and causing a stream of gaseous oxygen saturated with water to bubble through the solvent in the flask by way of a glass tube having a diameter of 3 mm. at a speed of 10 to 12 bubbles per minute; a 1/2 x 2 x 1/8 inch SAE steel strip is suspended in the vapor phase while a 1/4 x 3/4 x 1/16 inch SAE steel strip is introduced into the flask in the liquid phase; a 150 w. frosted light bulb is used both as a light and heat source and placed underneath the flask.

At the end of the test, the acidity of the trichloroethylene is determined. The percentages of the various adjuvants are given by weight. The pH values are determined in the aqueous extracts of trichloroethylene after the completion of the stability test by using in each case the same ratio of water:trichloroethylene of 1:1. All of the tests were repeated two or three times and the results averaged.

TEST SERIES I

Examples 1-15

This test series was conducted to demonstrate the stabilizing action of the synergetic mixture of butylene oxide and isobutyl alcohol+phenol+N,N-dimethylhydrazine. Table I shows the results of the tests on the basis of Examples 1 through 15: Examples 1 to 4 were carried out with individual stabilizing compounds; Examples 5 to 10 with binary mixture, Examples 11 to 14 with ternary mixtures and Example 15 finally with the quaternary mixture according to our present invention.

It will be noted from the results shown in Table I that the pH value of the trichloroethylene samples stabilized with individual stabilizing compounds or with binary and ternary mixtures is much lower than 7.0 and thus noticeably acid, whereas the pH value of the sample stabilized with the quaternary mixture of butylene oxide+isobutyl alcohol+phenol+N,N-dimethylhydrazine remains practically neutral after the completion of the stability test.

TABLE I

Sample No.	Stabilizers added to trichloroethylene	pH of trichloroethylene after accelerated oxidation test
1-----	N,N-dimethylhydrazine 0.01%-----	2.1-2.4
2-----	Butylene oxide 0.2%-----	1.7-2.0
3-----	Isobutyl alcohol 0.07%-----	1.7-2.0
4-----	Phenol 0.01%-----	2.0-2.3
5-----	N,N-dimethylhydrazine 0.01%+butylene oxide 0.2%-----	2.3-2.6
6-----	N,N-dimethylhydrazine 0.01%+isobutyl alcohol 0.07%-----	2.3-2.6
7-----	N,N-dimethylhydrazine 0.01%+phenol 0.01%-----	2.5-2.8
8-----	Butylene oxide 0.2%+isobutyl alcohol 0.07%-----	3.1-3.4
9-----	Butylene oxide 0.2%+phenol 0.01%-----	2.2-2.6
10-----	Isobutyl alcohol 0.07%+phenol 0.01%-----	2.2-2.6
11-----	N,N-dimethylhydrazine 0.01%+butylene oxide 0.2%+isobutyl alcohol 0.07%-----	3.8-4.1
12-----	N,N-dimethylhydrazine 0.01%+butylene oxide 0.2%+phenol 0.01%-----	3.4-3.7
13-----	N,N-dimethylhydrazine 0.01%+isobutyl alcohol 0.07%+phenol 0.01%-----	3.2-2.6
14-----	Butylene oxide 0.2%+isobutyl alcohol 0.07%+phenol 0.01%-----	2.5-2.8
15-----	N,N-dimethylhydrazine 0.01%+butylene oxide 0.2%+isobutyl alcohol 0.07%+phenol 0.01%-----	6.6-7.0

TEST SERIES II

Examples 16-30

Tests 16 through 30 were conducted to prove the stabilizing action of the synergetic mixture of propylene oxide+isobutyl alcohol+orthonitrophenol+N,N-dimethylhydrazine. The results obtained are indicated in Table II below and demonstrate clearly the same fact that also Test Series I and Table I show, i.e. that only the pH value of the sample stabilized with the above-given synergetic quaternary mixture remains practically neutral after the accelerated oxidation test, whereas all the other samples stabilized with either individual stabilizers or binary or even ternary combinations of the same become decidedly acid after the same oxidation test.

TABLE II

Sample No.	Stabilizers added to trichloroethylene	pH of trichloroethylene after accelerated oxidation test
16-----	N,N-dimethylhydrazine 0.01%-----	2.1-2.4
17-----	Propylene oxide 0.2%-----	1.9-2.2
18-----	Isobutyl alcohol 0.07%-----	1.7-2.0
19-----	o-Nitrophenol 0.01%-----	2.7-2.9
20-----	N,N-dimethylhydrazine 0.01%+propylene oxide 0.2%-----	2.1-2.4
21-----	N,N-dimethylhydrazine 0.01%+isobutyl alcohol 0.07%-----	2.3-2.6
22-----	N,N-dimethylhydrazine 0.01%+o-nitrophenol 0.01%-----	2.5-2.8
23-----	Propylene oxide 0.2%+isobutyl alcohol 0.07%-----	2.9-3.2
24-----	Propylene oxide 0.2%+o-nitrophenol 0.01%-----	1.9-2.2
25-----	Isobutyl alcohol 0.07%+o-nitrophenol 0.01%-----	2.0-2.2
26-----	N,N-dimethylhydrazine 0.01%+propylene oxide 0.2%+isobutyl alcohol 0.07%-----	3.7-4.0
27-----	N,N-dimethylhydrazine 0.01%+propylene oxide 0.2%+o-nitrophenol 0.01%-----	4.2-4.5
28-----	N,N-dimethylhydrazine 0.01%+isobutyl alcohol 0.07%+o-nitrophenol 0.01%-----	3.1-3.3
29-----	Propylene oxide 0.2%+isobutyl alcohol 0.07%+o-nitrophenol 0.01%-----	2.1-2.3
30-----	N,N-dimethylhydrazine 0.01%+propylene oxide 0.2%+isobutyl alcohol 0.07%+o-nitrophenol 0.01%-----	6.5-7.0

We claim:

1. A trichloroethylene composition stabilized against acidic decomposition, particularly during its use for degreasing metals, which comprises small quantities, intimately mixed and synergetically active, of N,N-dimethylhydrazine, isobutyl alcohol, butylene oxide, and phenol.

2. A stabilizing composition for trichloroethylene comprised of a synergetic mixture, of from about 1 to 100 portions by weight of N,N-dimethylhydrazine, from about 10 to 100 portions by weight of isobutyl alcohol, from about 1 to 100 portions by weight of phenol, and from 10 to 1000 portions by weight of butylene oxide.

3. A trichloroethylene composition stabilized against acidic decomposition, particularly during its use for the degreasing of metals, which comprises small quantities, intimately mixed and synergetically active, of N,N-dimethylhydrazine, isobutyl alcohol, propylene oxide and o-nitrophenol.

4. A stabilizing composition for trichloroethylene comprised of a synergetic mixture of from about 1 to 100 parts by weight of N,N-dimethylhydrazine, from about 10 to 100 parts by weight of isobutyl alcohol, from about 1 to 100 parts by weight of o-nitrophenol and from 10 to 1000 parts by weight of propylene oxide.

5. A method of stabilizing trichloroethylene for preventing its acidic decomposition, especially during the degreasing of metals, comprising the step of intimately mixing to the trichloroethylene small quantities of a synergetic quaternary mixture of N,N-dimethylhydrazine, isobutyl alcohol, butylene oxide and phenol.

6. A method of stabilizing trichloroethylene for preventing its acidic decomposition, especially during the degreasing of metals, comprising the step of intimately mixing to the trichloroethylene small quantities of a synergetic quaternary mixture of from about 1 to 100 parts by weight of N,N-dimethylhydrazine, from about 10 to 100 parts by weight of isobutyl alcohol, from about 1 to 100 parts by weight of phenol and from about 10 to 1000 parts by weight of butylene oxide.

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