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STABILIZATION OF LIQUID HALOGENATED ALIPHATIC HYDROCARBONS

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1 Claim. (Cl. 260—652.5)

This invention deals with the stabilization of liquid halogenated aliphatic hydrocarbons, especially chlorinated aliphatic hydrocarbons. It is more particularly concerned with the stabilization of chlorinated aliphatic hydrocarbon degreasing solvents.

Halogenated hydrocarbons such as trichloroethylene and perchloroethylene evidence strong decomposition tendencies during storage, use and shipment. In the presence of metallic surfaces such as iron, copper, zinc, aluminum and the alloys of such metals, this decomposition is often pronounced. Often the decomposition negates practical usefulness of the halogenated hydrocarbon. Frequently the commercial value of the halogenated hydrocarbon depends largely upon minimizing or avoiding serious decomposition.

Particularly acute decomposition problems arise in the use of trichloroethylene for degreasing of metals, especially aluminum. Unless adequately stabilized, trichloroethylene decomposes with alarming rapidity during degreasing usages. Not only does this decomposition destroy the usefulness of trichloroethylene as a degreasing solvent, but decomposition often is accompanied by the appearance of a tarry black intolerable residue that clogs and otherwise interferes with continued operation of the degreaser.

Effective stabilization of degreasing solvents, moreover, is complicated by the nature of degreasing operations. Degreasing entails utilizing a solvent in both liquid and vapor phases. In addition, commercial degreasers are operated for extended periods of time, often several months or longer, with a single charge of solvent except for some addition of makeup solvent. Solvent is thus repeatedly vaporized and condensed. Adequate stabilization must protect trichloroethylene against detrimental decomposition both in vapor and liquid phases and should continue to exert a stabilizing effect even after repeated distillations of trichloroethylene.

Now it has been discovered that liquid aliphatic halogenated hydrocarbons and especially chlorinated aliphatic hydrocarbons useful as degreasing solvents, notably trichloroethylene, may be stabilized by the use of small amounts of tetrahydrothiophene. Trichloroethylene containing as little as about 0.01 percent tetrahydrothiophene by weight or even less, accordingly, evidences substantial resistance to decomposition. Even under conditions of use encountered during degreasing of metals, trichloroethylene in which a small amount of tetrahydrothiophene has been dissolved manifests substantial resistance to decomposition.

While the stabilizing effects of tetrahydrothiophene is realized in trichloroethylene containing about 0.01 percent tetrahydrothiophene by weight, somewhat larger tetrahydrothiophene concentrations, notably at least 0.02 percent by weight of tetrahydrothiophene are preferable.

Normally, its concentration is 0.01 to 0.5 percent by weight of the trichloroethylene. Higher concentrations of tetrahydrothiophene up to 5 percent by weight of the trichloroethylene, or even greater concentrations, are operable. Costs rather than operability usually dictate use of the lower concentrations herein enumerated.

Since it may be expeditious to protect trichloroethylene against any and all detrimental effects, other additives may be used along with tetrahydrothiophene. Such additives may even augment the stabilizing effect of tetrahydrothiophene or retard other undesirable effects. Anti-oxidants and stabilizers useful for retarding decomposition caused by photoxidation may be included in the trichloroethylene without detracting from the stabilizing effect of tetrahydrothiophene.

Aromatic compounds containing a phenolic hydroxyl group linked directly to a ring carbon such as phenol, thymol, catechol, para-cresol, guaicol, methyl salicylate, eugenol, isoeugenol and the like may be included in the trichloroethylene when tetrahydrothiophene is present. As a rule, these phenols generally have normal boiling points on the order of 180° C. to 250° C.

Also a wide variety of amines may be included along with tetrahydrothiophene in trichloroethylene. Amines as a general class have been recognized to impart certain stabilizing qualities to the trichloroethylene. Their use in conjunction with tetrahydrothiophene does not interfere with the stabilizing effect of tetrahydrothiophene. Among the typical amines which may be used are diethylamine, triethylamine, dipropylamine, tripropylamine, triisopropylamine, dibutylamine, di-sec-butylamine, diisobutylamine, diisopropylamine, diethanolamine, triethanolamine, N-methylmorpholine, methylpyrrole, beta-picoline, pyridine, aniline and the like.

Other additives may be incorporated in trichloroethylene along with the tetrahydrothiophene. Organic 1,2-epoxides (or oxiranes) may be included. Typical of such epoxides are thylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, butadiene monoxide, butadiene dioxide, epichlorohydrin, glycidol, isobutylene oxide, 1,2-octylene oxide, 2,3-octylene oxide, 2,3-diisobutylene oxide, styrene oxide, cyclohexene oxide and cyclopentene oxide. Ethyl acetate or like organic esters of monocarboxylic acids, alcohols such as propynyl alcohol, methanol, ethanol, etc., olefinically unsaturated compounds such as diisobutylene and the like may be included.

As a general rule, the concentration in trichloroethylene of these various additives does not exceed 1 or 2 percent by weight. The individual concentration in which each each additive may be present is widely variable, but usually ranges between 0.001 and 0.5 percent by weight. Even then, judicious selection of the additive's concentration is advisable. For example, amine concentration of about 0.5 percent by weight or more is not advised because amines in such concentrations are corrosive to zinc and zinc is a material of construction in many degreasers.

The following example illustrates the stabilizing effect of tetrahydrothiophene on halogenated hydrocarbons:

EXAMPLE

Trichloroethylene containing tetrahydrothiophene was tested by accepted procedures to obtain the following data

which demonstrates the stability imparted by the presence of tetrahydrothiophene:

Table I

Stabilizer Composition	Concentration Percent by Weight of Trichloroethylene	Acidity Alkalinity [1]		Standard Stability				HCl Evolved
		pH	Titer	Hours	pH	Titer	Color	
Tetrahydrothiophene	0.01	6.7	0.1	72	7.4	0.6	light amber.	nil.
Butylene Oxide	0.25							
Tetrahydrothiophene	0.01	6.2	0.5	[2] 72	7.35	0.3	do	nil.
Thymol	0.01							
Glycidol	0.05							
Ethyl Acetate	0.25							
Diisobutylene	0.20							
Mixed Butylene Oxides	0.25							
Thiophene	0.01	6.7	0.4	72	3.7	4.5	very dark.	nil.
Butylene Oxide	0.25							

[1] This test consists of placing a 25 milliliter trichloroethylene sample in a beaker containing 25 milliliters of neutral distilled water and stirring while reading the pH with a meter in a glass calomel electrode. The material was titrated with 0.01 N-hydrochloric acid or 0.01 N sodium hydroxide until the neutral pH is reached. The milliliters of hydrochloric acid or sodium hydroxide required is the titer.

[2] Turned black only after 187–235 hours of continuous testing.

The standard stability test is designed to evaluate the efficiency of the stabilizer under especially rigorous conditions comparable to those found in shop usage. Procedurally, it involves placing 250 milliliter solution of 87.5 percent by volume of the trichloroethylene including the stabilizer in 12.5 volume percent Houghton H3105 drawing oil (sold by E. F. Houghton and Company) in a narrow mouth flask. Five grams of zinc and 5 grams of aluminum chips are added and the solution refluxed for the reported time period passing one bubble per second of air at 25° C. saturated with water through the solution.

The solution is observed for color. At the end of the 72 hours, a 25 milliliter portion of the trichloroethylene is titrated for acidity-alkalinity as described heretofore. The evolution of any HCl is determined by passing uncondensed gases leaving the refluxing condenser into a nitric acid acidulated silver nitrate fluid.

The test data reported in Table I above indicates extremely effective stabilization of trichloroethylene under conditions representative of the most vigorous encountered in the normal use of trichloroethylene. The pH and titer of the trichloroethylene remains surprisingly constant despite the severity of the test conditions.

Additionally, the fact that the stabilized samples, see footnote (2) of the table above, turned black only after some 200 hours of continuous testing under the standard stability test conditions is indicative of the highly effective stabilization of trichloroethylene achieved by the stabilizing compositions including tetrahydrothiophene.

Moreover, the data in Table I demonstrates the unexpected and important stabilizing qualities of tetrahydrothiophene. Thus, comparison of the data obtained employing thiophene in lieu of tetrahydrothiophene in conjunction with butylene oxide indicates the stabilizing action of tetrahydrothiophene. When thiophene was employed in lieu of tetrahydrothiophene, trichloroethylene tested under standard stability test conditions rapidly developed a highly acidic pH and showed an increased titer. Increased acidity titer indicates ineffective stabilization of trichloroethylene.

Use of tetrahydrothiophene alone or in conjunction with other additives is of general applicability respecting the stabilization of all normally liquid halogenated hydrocarbons of 1 to 3 carbon atoms. Tetrahydrothiophene is particularly useful for stabilizing trichloroethylene, particularly when trichloroethylene is used as a degreasing solvent. Nevertheless, tetrahydrothiophene may be used to impart stabilizing qualities to various other chlorinated aliphatic hydrocarbons including methyl chloride, ethylene chloride, perchloroethylene, and 1,1,1-trichloropropane.

Although this invention has been described by reference to specific details of certain embodiments, it is not intended that the invention be construed as limited to such specific details except insofar as such details appear in the appended claim.

I claim:

A liquid composition comprising trichloroethylene containing in cooperative stabilizing concentration tetrahydrothiophene and butylene oxide.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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William R. Dial

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 53, strike out "each"; columns 3 and 4, Table I, column 1 of the table should appear as shown below instead of as in the patent:

Stabilizer Composition
Tetrahydrothiophene------
Butylene Oxide----------
Tetrahydrothiophene------
Thymol----------
Glycidol----------
Ethyl Acetate----------
Diisobutylene----------
Mixed Butylene Oxides----
Thiophene----------
Butylene Oxide----------

Signed and sealed this 25th day of December 1962.

(SEAL)
Attest:

ERNEST W. SWIDER

Attesting Officer

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Patents