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CHLORINATED HYDROCARBON COMPOSITIONS

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2 Claims

ABSTRACT OF THE DISCLOSURE

Stable chlorinated hydrocarbon compositions are prepared by adding to the chlorinated hydrocarbon an amine of the general formula $H_2N-A-NH_2$, where A is a bivalent aliphatic alkyl radical with 2-3 C atoms, together with pyrrole or N-methyl-pyrrole.

This invention relates to stabilizing chlorinated hydrocarbons and it has for its object to provide a novel and improved process for this purpose.

Another object of the invention is to enable chlorinated hydrocarbons to be effectively stabilized by the addition thereto of very small quantities of specific compounds hereinafter described.

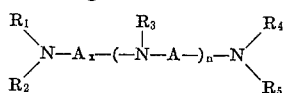
Numerous solvents are used for degreasing metals, for dry cleaning and for extraction purposes. Among these the unsaturated chlorinated aliphatic hydrocarbons are preferred because of their high solvent effect and their incombustibility, especially, for instance, trichlorethylene. However, the advantage of their strong solvent effect is offset by the drawback of their poor stability which makes their use without prior stabilization very difficult.

The decomposition of trichlorethylene, for instance, is caused by light and oxygen and is catalyzed by heat and contact with metals. Therefore small quantities of additives are used to stabilize the trichloroethylene or to neutralize the hydrogen chloride formed during decomposition. Particularly valuable additives are acid-binding substances, like the basic amines which are customarily used to keep trichlorethylene under alkaline conditions.

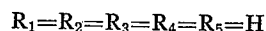
In order to retard oxidation it has also been suggested to use small quantities of alcohols, phenols, N-alkyl pyrroles or epoxy compounds.

It is also known that the simultaneous addition of an alcohol and of certain amines gives the chlorinated hydrocarbons good stability against daylight.

We have now discovered that chlorinated hydrocarbons can be stabilized effectively by adding diamines, triamines or polyamines of the general formula



to the chlorinated hydrocarbon either singly or in mixtures. The letters in this formula represent:



aliphatic alkyl radical with 1-3 carbon atoms, hydroxy alkyl radical with 1-3 carbon atoms or hydrogenated heterocyclic radical with 4-5 carbon atoms; A=bivalent

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aliphatic unsaturated alkyl radical with 2-3 carbon atoms or phenylene radical; $x=1-4$; and $n=0-4$.

The addition of 0.001-0.02 weight percent of these compounds (referred to the chlorinated hydrocarbon) to the chlorinated hydrocarbon to be stabilized, e.g. dichlorethylene, trichlorethylene, perchlorethylene, increases their resistance against iron and aluminum.

By using diamines, e.g. ethylene diamine, trimethylene diamine, triethylene diamine, 1,2-di-(N,N-morpholine-) ethane, 1,2-di-(N,N-piperidine-) ethane, or triamines, e.g. diethylene triamine, or polyamines, e.g. tetraethylene pentamine, it is possible to obtain an excellent stabilizing effect. This can be increased by the addition of aliphatic monoamines, e.g. diisopropyl amine or pyrrole or N-alkyl pyrroles, e.g., N-methyl pyrrole. It has been found that even quantities of 0.002-0.005 weight percent, referred to the chlorinated hydrocarbon, have a surprising effect.

The tabulated results of the stabilizing effects show clearly the high degree of stabilization achieved by our invention. The stabilizing effect of various diamines, triamines and polyamines which are used to improve the resistance of, for instance, trichlorethylene against decomposition by light and oxygen, is proven by the accelerated oxidation test as per MIL-T-7003 or Federal Specification OT-634/a, which is carried out as follows:

200 ml. of the trichlorethylene sample are placed in a retort. A steel strip measuring $\frac{1}{2}'' \times 2'' \times \frac{1}{16}''$ is hung up with a copper wire in the reflux condenser and another steel strip measuring $\frac{1}{4}'' \times \frac{3}{4}'' \times \frac{1}{16}''$ is placed on the bottom of the retort. The input pipe for the water-saturated oxygen must reach down to within $\frac{1}{4}''$ from the bottom of the retort. The diameter and immersion depth of the pipe below the water surface for controlling the pressure of the oxygen are fixed in such a manner that a stream of oxygen of about 10-12 bubbles per minute, measured by a bubble counter, is produced. The heat source is a frosted lamp of 150 watts which is mounted underneath the retort. After 48 hours of reflux a sample is drawn, it is allowed to cool to room temperature and the acidity of the sample is then determined in an aqueous extract by titration with 0.1 N NaOH against phenolphthalein as the indicator. After a 48 hour test the acidity must not exceed the value of 0.02 weight percent HCl, referred to trichlorethylene.

Example 1

4 samples of 200 ml. trichlorethylene which is stabilized with 0.004 weight percent ethylene diamine are refluxed in a water-saturated oxygen stream, a frosted lamp of 150 watts serving as the heat source. Small steel plates are mounted in the liquid and in the vapor phase. A sample is drawn after 48 hours and, after the sample has cooled, the acid components are extracted with 25 ml. water. The aqueous extract is then titrated with 0.1 N NaOH against phenolphthalein as an indicator to determine the acidity of the sample. After a 48 hour test treatment the sample is still alkaline. The heating is stopped when the acidity has exceeded the limit of 0.02 weight percent HCl, referred to trichlorethylene. In the case of 4 samples 0.020, 0.017, 0.021 and 0.019 weight percent HCl were titrimetrically determined after 240 hours of refluxing, or an average of 0.019 weight percent HCl. Thus after 240 hours of refluxing the acidity limit is not yet exceeded.

TABLE 1

Test No.	Additive (mg./kg. trichlorethylene)	Acidity (percent HCl) after 48 hrs.	Duration (hours)	Acidity (percent HCl)
1			1	0.024
2			48	0.089
3	Di-isopropylamine (40)	0.089	96	0.044
4	Di-isopropylamine (100)	0.008	188	0.055
5	Di-isopropylamine (200)	0.003	240	0.019
6	Ethylenediamine (40)	Alkaline	480	0.011
7	Ethylenediamine (200)	do	336	0.014
8	Triethylenediamine (200)	do	504	0.011
9	Trimethylenediamine (200)	do	456	0.011
10	1,2-propylenediamine (200)	do	240	0.022
11	N,N,N'-triethylethylenediamine (200)	Under 0.001	312	0.013
12	N,N,N',N'-tetramethylethylenediamine (200)	do	528	0.015
13	N,N-dimethylethylenediamine (200)	Alkaline	216	0.020
14	Diethylenetriamine (200)	Under 0.001	144	0.015
15	Tetraethylenepentamine (200)	do	336	0.004
16	1,2,4-trimethylpiperazine (200)	Alkaline	264	0.010
17	N-oxethylpiperazine (200)	Under 0.001	168	0.019
18	1,2-di-(N,N-morpholine) ethane (200)	do		

The results of tests 5, 6, 7, 8 and 9 show the considerably stronger inhibiting effect of a diamine over that of a monoamine (tests 2, 3, 4). The table also shows that ethylene diamine (tests 5, 6) and trimethylene diamine (test 8), i.e. the simple aliphatic non-substituted diamines have the best effect.

Example 2

In a test made in accordance with Example 1, 200 ml. trichlorethylene with an additive of 0.004 weight percent diisopropylamine and 0.004 weight percent ethylene diamine are refluxed for 48 hours. After that period, and even after 450 hours' heating the test is still alkaline.

Example 3

We proceed as in Example 1, using small iron plates, where each time 20 ml. trichlorethylene are used to which stabilizing mixtures are added. The trichlorethylene which has been prepared in such a manner is then treated for several hours under reflux in a water-saturated oxygen stream. Table 2 shows the results of these tests.

TABLE 2

Test No.	Additive (mg./kg. trichlorethylene)	Acidity (Percent HCl) after 48 hrs.	Duration (hours)	Acidity (percent HCl)
1	Di-isopropylamine (40)	Alkaline	192	0.019
2	Ethylenediamine	do	450	(¹)
3	Di-isopropylamine (40)	do		
4	Ethylenediamine (40)	0.015	52	0.080
5	Di-isopropylamine (30)	0.005	168	0.023
6	N-methylpyrrole (80)	Alkaline	432	0.001
7	Ethylenediamine (30)	do	816	0.010
8	N-methylpyrrole (30)	0.003	264	0.029
9	Di-isopropylamine (100)	Alkaline	830	0.023
10	Ethylenediamine (30)	do	508	0.017
11	Di-isopropylamine (30)	0.011	96	0.038
12	Fyrrole (50)	Alkaline	312	0.009
13	Ethylenediamine (30)	do		

¹ Alkaline.

The test results shown in Table 2 demonstrate the synergism of the combinations ethylene diamine/N-

methyl pyrrole and pyrrole and di-isopropylamine/ethylene diamine. The table shows that the effect of the addition of 0.003 weight percent ethylene diamine and 0.01 weight percent N-methyl pyrrole to trichlorethylene during the oxidation test results in a resistance of trichlorethylene of more than 800 hours. Furthermore, the combination of di-isopropylamine/N-methyl pyrrole shows an acidity content of 0.08% HCl after 52 hours heating, while for the combination ethylene diamine/N-methyl pyrrole after 432 hours an acidity of only 0.001% HCl is found.

The invention claimed is:

1. A chlorinated hydrocarbon selected from the group consisting of dichlorethylene, trichlorethylene and perchlorethylene containing from 0.001 to 0.02 weight percent, related to said chlorinated hydrocarbon, of an amine selected from the group consisting of ethylene diamine, trimethylene diamine and 1,2-propylene diamine, and 0.005 to 0.01 weight percent, related to said chlorinated hydrocarbon, of a substance selected from the group consisting of pyrrole and N-methyl pyrrole.
2. A process for inhibiting the decomposition of a chlorinated hydrocarbon selected from the group consisting of dichlorethylene, trichlorethylene and perchlorethylene during contact with metals which comprises maintaining dissolved therein from 0.001 to 0.02 weight percent of an amine selected from the group consisting of ethylene diamine, trimethylene diamine and 1,2-propylene diamine, and 0.005 to 0.01 weight percent of a substance selected from the group consisting of pyrrole and N-methyl pyrrole.

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