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INHIBITOR FOR CHLORINATED SOLVENTS

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This invention relates to the stabilization of chlorinated aliphatic hydrocarbons against decomposition and the improved composition of matter obtained thereby, as well as to a method of inhibiting the corrosive action of chlorinated aliphatic hydrocarbons upon metal surfaces in contact therewith.

The marked tendency of chlorinated aliphatic hydrocarbons, e. g. carbon tetrachloride, tetrachloroethylene, propylene chloride, etc., to undergo decomposition during storage and/or distillation, particularly in the presence of moisture, is well known. Such decomposition, when it occurs, imparts to the chlorinated hydrocarbons corrosive properties which render them objectionable for many purposes.

We have now found that chlorinated aliphatic hydrocarbons can be rendered stable during storage and/or distillation by incorporating therewith a relatively small amount of a piperazine compound. We have also found that the addition of a piperazine compound to such chlorinated solvents results in stabilizing these materials against decomposition in sunlight. The term "piperazine compound" as hereinafter employed refers to any compound containing the piperazine nucleus. The invention, then, consists in the stabilization of chlorinated aliphatic hydrocarbons, in the improved composition obtained by such stabilization, and to a method of inhibiting the corrosive action upon metal surfaces of unstabilized chlorinated aliphatic hydrocarbons in contact therewith, hereinafter fully described and particularly pointed out in the claims.

In the practice of our invention we add a relatively small percentage of a piperazine compound, such as tetramethyl piperazine or piperazine hydrate, to the chlorinated aliphatic hydrocarbon, preferably during manufacture or directly after the material has been purified by distillation. The proportion of the piperazine compound which we have found sufficient in admixture with chlorinated aliphatic hydrocarbons to suppress decomposition is relatively small, generally between about 0.01 and 1.0 per cent by volume. A greater percentage of stabilizing agent may be employed in instances where the corrosion rate of the chlorinated hydrocarbon is found to be greater than normal, or where the stabilizing agent is added to material already somewhat decomposed.

The following table shows the results which have been obtained in practicing our invention, using tetramethyl piperazine and piperazine hydrate for stabilizing against decomposition of certain chlorinated aliphatic hydrocarbons in contact with various metals. As a measure of the decomposition occurring in a chlorinated aliphatic hydrocarbon during contact with the metal, we have determined the weight of metal corroded away per unit area under refluxing conditions for 24 hours in the presence of water. The tests were conducted by immersing a weighed and measured strip of metal in 50 milliliters of chlorinated hydrocarbon and 20 milliliters of water, in a round-bottomed flask connected with a refluxing column, and heated under refluxing conditions. Thereafter the metal strips were re-weighed and the corrosion rate computed in milligrams per square inch of exposed metal area per day.

Table

Run No.	Solvent	Inhibitor employed	Quantity of inhibitor used	Metal	Corrosion rate gms./sq. in./24 hours
			cc.		
1	Tetrachloroethylene	None		Iron	14.9
2	do	Tetramethyl piperazine.	0.05	do	2.7
3	do	do	0.1	do	2.2
4	do	None		Copper	23.3
5	do	Tetramethyl piperazine.	0.05	do	4.6
6	do	do	0.10	do	4.2
7	do	None		Nickel	1.96
8	do	Tetramethyl piperazine.	0.05	do	0.64
9	do	do	0.01	do	0.56
10	do	None		Galv. iron	16.2
11	do	Tetramethyl piperazine.	0.05	do	5.8

Run No.	Solvent	Inhibitor employed	Quantity of inhibitor used	Metal	Corrosion rate gms./sq. in./24 hours
			cc.		
12	Tetrachloroethylene	Tetramethyl piperazine	0.10	Galv. iron	6.0
13	do	None		Zinc	34.1
14	do	Tetramethyl piperazine	0.05	do	15.0
15	do	do	0.10	do	16.0
16	do	None		Tin—iron	1.2
17	do	Tetramethyl piperazine	0.05	do	0.68
18	do	do	0.10	do	0.82
19	Carbon tetrachloride	None		Iron	75.44
20	do	Tetramethyl piperazine	0.05	do	61.88
21	do	do	0.10	do	42.04
22	do	None		Nickel	0.88
23	do	Tetramethyl piperazine	0.05	do	0.20
24	do	do	0.10	do	0.24
25	do	None		Tin—iron	2.24
26	do	Tetramethyl piperazine	0.05	do	0.96
27	do	do	0.10	do	0.64
28	Ethylene chloride	None		Iron	4.40
29	do	Tetramethyl piperazine	0.05	do	2.28
30	do	None		Copper	2.96
31	do	Tetramethyl piperazine	0.05	do	0.40
32	Propylene chloride	None		Iron	3.44
33	do	Tetramethyl piperazine	0.05	do	1.80
34	do	None		Copper	0.80
35	do	Tetramethyl piperazine	0.05	do	0.16
36	Trichloroethylene	None		Iron	3.00
37	do	Tetramethyl piperazine	0.05	do	0.64
38	do	None		Copper	1.52
39	do	Tetramethyl piperazine	0.05	do	0.40
40	Tetrachloroethylene	None		Iron	11.0
41	do	Piperazine hydrate	0.10	do	1.24
42	do	None		Copper	29.12
43	do	Piperazine hydrate	0.10	do	5.44

From the above table it will be seen that the corrosion rate of hot, moist chlorinated solvents upon the commonly used metals may be reduced very materially by the addition of less than one per cent of a simple compound of piperazine.

To illustrate the stabilizing effect obtained by adding a piperazine compound to commercial chlorinated solvents which are to be subjected to the influence of light, we have exposed samples of both stabilized and unstabilized solvents to the action of ultra-violet light rays for 24 hour periods, and subsequently determined the extent of the resultant decomposition. A test demonstrating the extent of the decomposition is afforded by washing the solvent under test with caustic alkali, neutralizing the mixture, and titrating the same with tenth-normal silver nitrate for reactive chlorine. Thus, when 4 samples of tetrachloroethylene which had been subjected to the rays of a sun-lamp for 24 hours were tested, it was found that 50 milliliters of unstabilized material required the addition of 14.2 milliliters of silver nitrate to precipitate the free chlorine therein, while 50 milliliters of material stabilized by the addition of 0.2 per cent by volume of tetramethyl piperazine required only 0.15 milliliter of silver nitrate. These results indicate that tetrachloroethylene stabilized by the addition of a minute amount of tetramethyl piperazine contains only about 1.2 per cent of the quantity of decomposition products contained in an equal quantity of unstabilized tetrachloroethylene.

If desired, piperazine itself may be employed in place of a derivative thereof, but it is believed that piperazine, when added to an aqueous solvent, is immediately converted to piperazine hydrate and the latter compound becomes the stabilizing agent.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the materials employed, provided the step or material mentioned in any of the following claims or equivalents of such stated step or material be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A chlorinated aliphatic hydrocarbon containing a relatively small amount of tetramethyl piperazine.

2. A composition of matter comprising tetrachloroethylene containing a relatively small amount of tetramethyl piperazine.

3. A composition of matter comprising carbon tetrachloride containing a relatively small amount of tetramethyl piperazine.

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