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STABILIZATION OF CHLORINATED HYDROCARBONS WITH NITRILES

Fred S. Hirsekorn and John H. Rains, Wichita, Kans., assignors to Frontier Chemical Company, Division of Vulcan Materials Company, Wichita, Kans., a corporation of New Jersey

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This invention relates to the stabilization of halogenated aliphatic hydrocarbons such as perchlorethylene and to the stabilized composition, the stabilizer being selected from the group consisting of 3-butenenitrile, methacrylonitrile, and mixtures thereof.

It is known that chlorinated hydrocarbons such as perchlorethylene have a tendency to decompose during storage, shipment and sometimes use. This tendency becomes more pronounced when the chlorinated hydrocarbon is in contact with metals such as copper, steel, aluminum, brass, etc., and/or is exposed to heat, moisture and light. Such decomposition results in the formation of hydrogen chloride and phosgene, among other objectionable decomposition products. These may cause serious corrosion of metal in dry cleaning machines and metal degreasing units. The acidic products of decomposition may be detrimental to fabrics and to many dyes. Consequently, materials which will inhibit or prevent the decomposition of these chlorinated hydrocarbons are usually added.

In a broad embodiment the present invention comprises adding to a chlorinated hydrocarbon such as perchlorethylene, a small but effective amount of a stabilizer comprising 3-butenenitrile, methacrylonitrile, and mixtures thereof. The stabilizers may be added in proportions from about 0.005% to about 1.0% by weight of the chlorinated hydrocarbon although as a rule the stabilizers are not required in amounts exceeding about 0.2% to 0.5%.

Perchlorethylene is the chlorinated hydrocarbon with which the invention is most particularly concerned although it is also applicable to other chlorinated hydrocarbons such as chloroform, methylene chloride, dichlorethylene, trichlorethylene and the like.

The chlorinated hydrocarbons containing from one to four carbon atoms are widely used as solvents in industry. The lower boiling liquid chlorinated hydrocarbons such as perchlorethylene are widely used in the dry cleaning industry where the problem of decomposition of the solvent may become acute due to corrosion of equipment and adverse effect upon the garments cleaned. In the examples which are set forth herein the effectiveness of the stabilizer was determined according to Method N.I.D. Specification 3–55 of the National Institute of Dry Cleaners. Briefly, this method consists of refluxing perchlorethylene or other halogenated hydrocarbon under test, in a flask in the presence of water and strips of copper. One hundred ml. of the stabilized perchlorethylene is measured into a 300 ml. round bottom flask and 0.2 ml. of distilled

water is added. Strips of electrolytic copper 2.0 x 7.5 x 0.005 cm. are thoroughly cleaned and weighed. One strip is inserted in the flask so as to be substantially completely immersed in the liquid. A Soxhlet extractor having a volume of approximately 70 ml. is attached to the flask and a second copper strip is inserted into the extractor. A small Allihn condenser is mounted on top of the Soxhlet extractor and a third copper strip is placed in the condenser so that the perchlorethylene condenses on the strip. A 100 watt frosted Mazda incandescent light bulb is placed one inch from the extractor vapor tube to supply energy for photochemical oxidation. The flask is heated by suitable means so as to reflux the composition at a rate which causes the extractor to empty about once every eight to ten minutes. These conditions are maintained for the duration of the test which is usually 24 hours but may be longer. The condenser is attached to a water scrubber to absorb any hydrogen chloride which may be evolved during the test.

After the test is complete the flask is cooled and a quantity of water equal to the perchlorethylene sample is poured through the condenser and extractor into the flask to absorb any acid. The contents of the flask are shaken and the acidity developed during the test is determined by sodium hydroxide titration using bromothymol blue as the indicator.

The loss in weight in milligrams of the copper strips suspended in the flask, extractor and condenser are determined and totaled. According to paragraph 14 of the N.I.D. specification 3–55 a maximum loss of 90 mg. (0.001 grams per square centimeter exposed) is permissible. As a practical matter for satisfactory commercial stabilization of the dry cleaning solvents such as perchlorethylene, the loss should be less than about 10 mg. over a 24 hour exposure period for satisfactory stabilizer performance.

In view of the fact that the perchlorethylene or other solvent is recovered by distilling it so as to separate the materials extracted during the dry cleaning operation, the stabilizer should boil in a range such that it will pass overhead with the solvent during the distillation. It should leave no spots or stains on fabrics after the solvent has been completely evaporated following completion of the dry cleaning cycle. The color of the stabilized solvent must remain water white after stabilization and after the recovery step. The residue after solvent evaporation must be below about 0.016 gram per 100 ml. of solvent. Preferably the stabilizer should be stable and should stabilize the chlorinated hydrocarbons against decomposition both in dark storage and when exposed to light.

In Table I are shown the results of tests using the above described method in which perchlorethylene only was used and perchlorethylene was tested using from about 0.005 to approximately 0.1% of methacrylonitrile. The test period was twenty-four hours with the exception of one test which was carried out for a period of 72 hours. In one test the perchlorethylene also contained about 1.0% of a commercial detergent which was Vividol-LT.

TABLE I

Weight Percent Methacrylonitrile	Duration of Test, Hours	pH		Acidity, p.p.m.	Weight Loss—Milligrams			
		Before	After		Flask	Extractor	Condenser	Total
0	24	7.6	2.1	382	5.9	6.1	[1] 207.3	219.3
0.0050	24	------	------	33	2.8	8.2	27.2	38.2
0.0102	24	------	------	0	0.6	0.7	1.3	2.6
0.0198	24	------	------	0	0.4	1.5	1.2	3.1
0.0500	24	------	------	0	0.3	0.7	1.6	2.6
0.0500	72	7.5	7.3	0	0.5	4.3	1.9	6.7
0.0701	24	7.4	7.3	0	0.5	1.0	1.7	3.2
0.0701 [2]	24	------	------	----------	1.5	1.1	1.7	4.3
0.1008	24	------	------	0	0.6	1.0	1.8	3.4

[1] Copper strip badly corroded.
[2] 1% detergent.

The data in Table I establish that methacrylonitrile is effective in reducing the copper corrosion according to the standard N.I.D. test in proportions of 0.005% to approximately 0.1%. Larger amounts of the stabilizer could be used but normally it is not required.

In concentrations of above about 0.01% the weight loss of the copper strips was reduced well below 10 mg. and in fact was well below 5 mg. for the 24 hour test and only slightly above that for the 72 hour test period.

Methacrylonitrile also stabilizes other halogenated hydrocarbons. Freshly prepared chloroform was stored for a two-week period in one liter clear glass bottles with and without a clean steel coupon and with and without methacrylonitrile in proportions of 200 p.p.m. The averages of acidity measured as HCl were as follows: With no stabilizer and without the steel coupon acidity averaged 0.125%, and with the stabilizer=0.014%. In the presence of a steel coupon the control sample averaged 0.144% and the methacrylonitrile stabilized sample averaged 0.061%. Two samples of each were stored. This shows that decomposition of chloroform was increased by the presence of the steel coupon but that the amount of decomposition was substantially reduced in the presence of methacrylonitrile.

In Table II are shown the results of a series of tests using 3-butenenitrile in proportions from approximately 0.005% to about 0.1% over a 24 hour test period using the N.I.D. procedure described above. In one instance 1.0% of the commercial detergent Vividol-LT was used.

TABLE II

3-Butenenitrile

Weight Percent	pH		Acidity, p.p.m.	Weight Loss, mg.			
	Before	After		Flask	Extractor	Condenser	Total
0	7.6	2.1	382	5.9	6.1	207.3	219.3
0.0047	7.2	2.6	75	2.3	8.2	64.2	74.7
0.0161			0	1.1	2.5	3.1	6.7
0.0500	7.6	7.4	0	0	0.7	0.2	0.9
0.0700	7.2	6.2	0	0.3	1.9	1.5	3.7
0.0700 [1]			0	0.9	1.3	1.1	3.3
0.1000			0	0.3	1.1	0.6	2.0

[1] Contained 1% detergent.

The results show that in proportions above about 0.005% the 3-butenenitrile prevented the formation of acidity and reduced the loss of weight of the copper strip to well below 10 mg.

3-butenenitrile likewise has been found to inhibit decomposition of chloroform both in the presence and in the absence of a steel coupon. The control samples with and without the steel coupon are given above, with 3-butenenitrile in the proportion of 200 p.p.m. by weight of the chloroform averaged 0.0051% without the coupon and 0.051% in the sample containing the steel coupon.

Ordinarily the stabilizer is added at the point of manufacture and packaging of the perchlorethylene. It is added before any substantial decomposition takes place. The finished composition is usually shipped to its destination in bulk, for example, in 55-gallon drums, in tank cars, or in trucks, although frequently smaller containers may be used. The stabilizers of this invention do not impart objectionable odor or color to the stabilized composition.

We claim as our invention:

1. A stabilized low-boiling chlorinated hydrocarbon selected from the group consisting of perchlorethylene and chloroform containing a small but effective amount of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile and mixtures thereof, the proportions of said stabilizers being about 0.005% to about 1.0%.

2. Stabilized perchlorethylene containing about 0.005% to about 1.0% of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile and mixtures thereof.

3. A method for stabilizing halogenated hydrocarbon selected from the group consisting of perchlorethylene and chloroform from decomposition under conditions of storage and use which comprises adding thereto a small but effective amount of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile and mixtures thereof, the proportions of said stabilizers being about 0.005% to about 1.0%.

4. A method for stabilizing perchlorethylene from decomposition under conditions of storage and use which comprises adding thereto about 0.005% to about 1.0% of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile, and mixtures thereof.

5. A method for stabilizing chloroform from decomposition under conditions of storage and use which comprises adding thereto about 0.005% to about 1.0% by weight of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile, and mixtures thereof.

6. Stabilized chloroform containing about 0.005% to about 1.0% by weight of a stabilizer selected from the group consisting of 3-butenenitrile and methacrylonitrile, and mixtures thereof.

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