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STABILIZED CHLOROHYDROCARBON SOLVENT COMPOSITION

Lawrence Fullhart, Jr., Newark, and Donald A. Swalheim, Hockessin, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This application is a continuation-in-part of our earlier application, Ser. No. 72,590, filed November 30, 1960, and now abandoned.

This invention relates to the stabilization of chlorohydrocarbons, particularly trichloroethylene and perchloroethylene. More particularly, this invention relates to the inhibition of corrosive chloride formation when a chlorohydrocarbon solvent is in contact with metallic surfaces under acidic conditions.

Chlorohydrocarbon compounds are extensively employed in industrial uses such as, for example, in metal cleaning and degreasing operations. These compounds are seldom used in their pure state for such industrial applications, since it is well recognized that such materials are susceptible to decomposition by heat, light, and oxygen under the usual conditions of storage and utility. Many compounds have been proposed by the prior art as stabilizers which, when added to chlorohydrocarbon compounds in small amounts, are useful in retarding this normal type of decomposition.

However effective these stabilizers may be, it has been found that chlorohydrocarbons containing the same in the course of their use decompose resulting in the formation of acids and a build-up of a significant acid content in the solvent. In addition to this mechanism which inherently promotes acid conditions, there are other instances in systems using chlorohydrocarbon solvents when acids are inadvertently introduced such as fatty acids present on workpieces to be degreased or when acids are deliberately introduced such as in an anhydrous phosphatizing bath. An acid condition developed by one or more of such means has the effect of initiating a further decomposition of the chlorohydrocarbon through a mechanism believed to be entirely different from the decomposition resulting from a simple oxidation of such solvents by atmospheric oxygen and results in the liberation of corrosive chlorides which present a serious corrosion problem to the workpieces and metal container which are in contact with the chlorohydrocarbon solvent. Although it is not intended to limit the present invention to any specific mechanism, it is believed that the acids present react with the workpieces in contact with the chlorohydrocarbon solvent forming hydrogen-free radicals which in turn attack the solvent causing its progressive deterioration with the resulting formation of corrosive chlorides. The stabilizers of the prior art useful to retard normal decomposition by heat, oxygen, and light are usually intended for neutral or basic conditions and, in general, are found to be ineffective to prevent such deterioration of chlorohydrocarbon solvents caused as a result of acid conditions.

Of course, it may be expected that the type of decomposition described above with its attendant corrosion problems will be particularly severe where the system

employing a chlorohydrocarbon solvent is of design an acidic medium. This has been found to be the case in actual practice and for this reason the present invention has particular utility in an anhydrous phosphatizing system employed in metal finishing operations as a desired means of applying phosphate coatings to metal surfaces to reduce corrosion and improve paint adhesion. In the execution of such a system, which is highly acidic, metallic surfaces are contacted with a composition consisting of a chlorohydrocarbon solvent as a primary component with a phosphatizing amount of phosphoric acid and an agent which solubilizes the phosphoric acid in the chlorohydrocarbon solvent. Broadly, a phosphatizing amount of phosphoric acid may be considered to be an amount between approximately 0.05% and 7.5% by weight based on the total weight of the bath. Preferably, the phosphatizing bath contains from 0.2% to 0.8% by weight of phosphoric acid. Representative of agents which may be used to solubilize phosphoric acid in the bath are a group of oxygen-containing solvents that are lower molecular weight aliphatic alcohols containing from 3 to 8 carbon atoms and alkyl acid phosphate compounds of the type obtainable by reacting phosphoric acid with an alcohol containing from 3 to 8 carbon atoms. Of these, the lower molecular weight alcohols, particularly the four-carbon and five-carbon alcohols, such as butyl and amyl alcohol, are preferred and based on the above-stated range of phosphoric acid, an amount of the alcohol in the range of from about 1% to about 40% can be used in the compositions, and from 1% to 10% by weight based on the total weight of the phosphatizing bath is preferred. In many instances, a combination of one of the above alcohols together with an acid phosphate ester derived by reacting phosphoric acid with said alcohol is particularly useful.

It has been found that anhydrous phosphatizing baths of this type may be conveniently employed as part of an integrated unit which also includes solvent degreasing and/or painting operations separated from the phosphatizing bath by suitable partitions but under a common vapor zone of the chlorohydrocarbon solvent. Due to the volatility of the hydrogen chloride and corrosive chlorides formed through the decomposition of the chlorohydrocarbon solvent by virute of the acid medium in the phosphatizing bath, corrosion in the metal container of such an integrated unit is not confined to the immediate vicinity of the phosphatizing bath but rather extends across the entire unit, particularly at the condensate region of the unit. Obviously, in order for the operation of such an integrated system to be commercially successful, decomposition of the chlorohydrocarbon solvent and the corrosion problems this decomposition present must be prevented.

It is, therefore, the object of the present invention to provide an agent which will effectively stabilize chlorohydrocarbon solvents so as to prolong their useful life.

It is a further object of the present invention to provide a stabilizing agent which will effectively inhibit the formation of corrosive chlorides when metallic workpieces are treated with chlorohydrocarbon solvents in an acidic medium.

In accordance with the present invention, the above objects and still other objects which will become clear from what is to follow are accomplished by adding to the chloro-

hydrocarbon solvent a small amount of a nitro aromatic compound as a stabilizing agent. In addition to being highly effective in stablizing chlorohydrocarbons under acid conditions, the agents of the present invention also provide protection against deterioration of chlorohydrocarbons from oxidation by heat, light, and oxygen. They may, therefore, be employed as the sole stabilizing system for chlorohydrocarbons, although it may be preferred to use them in combination with the various conventional stabilizers specifically proposed for retarding normal decomposition by heat, light, and oxygen.

Nitro aromatic compounds are cyclic organic compounds broadly which exhibit aromatic character substituted with a nitro or polynitro function. The compounds may be mononuclear or polynuclear and may contain various substituent groups other than the required nitro group or polynitro groups. It will be understood, of course, that the compounds should not contain groups (for example, peroxide groups) which might interfere with the desired function of the stabilizers or the systems in which they are to be employed. The aromatic character of the compounds for the present invention is preferably due to the presence of the benzene nucleus or nuclei as the case may be, but may also be due to a carbocyclic nucleus or nuclei other than benzene like indene or to a heterocyclic nucleus or nuclei such as pyridine or thiophene alone or in combination with a benzene nucleus or nuclei which are known to exhibit aromatic character. Non-limiting examples of these compounds suitable for purposes of present invention include nitrobenzene, m-dinitrobenzene, o-nitrotoluene, m-nitrotoluene, o-nitroethylbenzene, o-nitroisobutylbenzene, o-nitroanisole, p-nitroanisole, 2-nitro-4-aminoanisole, 3-nitro - 5 - aminoanisole, o-nitrochlorobenzene, p - nitrophenol, o - nitrophenol, 2,4-dinitrophenol, p-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 2,4-dinitrotoluene, 4-nitrotoluene-2 sulfonic acid, 3-nitrophthalic anhydride, o-nitrobiphenyl, 9-nitroanthracene, 1-nitronaphthalene, 2-nitrobenzamide, p-nitrophenylhydrazine, picrolonic acid (i.e., 3-methyl-4-nitro-1-p-nitrophenyl-5-pyrazolone, p - nitrophenylacetonitrile, m-nitrobenzyl alcohol, 5-nitroquinoline, 3-nitrodibenzofuran, dinitrocumene, and picric acid (2,4,6-trinitrophenol).

Nitro aromatic compounds of the type exemplified above, and as the term is used herein and in the ensuing claims, are defined as essentially aromatic compounds containing from 1 to 3 cyclic nuclei, having a molecular weight no greater than 225, and containing a substituted aromatic ring structure to which there is directly attached at least one nitro group.

Preferred stabilizers are those which contain at least two nitro groups in the same compound, at least two of said nitro groups being of the type which are bonded directly to an aromatic nucleus or ring structure. Examples of such compounds are dinitrobenzene, dinitrophenol, dinitrobenzoic acid, dinitrotoluene, picrolonic acid, dinitrocumene, and picric acid. These compounds may be used either as substantially pure single isomers, or, alternately, one may employ them in the form of the commercially available mixtures of isomers.

Combinations of two or more of the above compounds may advantageously be employed. Preferred combinations are those wherein at least two of the aromatic nitro compounds are employed, and each of the compounds has at least two nitro groups of the type which are bonded directly to an aromatic nucleus or ring structure. Examples of such preferred combinations are: dinitrotoluene plus dinitrobenzoic acid; dinitrocumene plus dinitrobenzoic acid; dinitrotoluene plus picric acid; dinitrocumene plus picric acid; dinitrobenzoic acid plus picric acid; dinitrotoluene plus dinitrobenzoic acid plus picric acid; and dinitrotoluene plus dinitrocumene plus picric acid.

The amount of the stabilizing agents hereof required to provide effective stabilization of chlorohydrocarbons is quite small and will vary to some extent with the individual compound. In general, an amount between 0.01% and 1% by weight based on the amount of chlorohydrocarbon will be preferred although some stabilization occurs even when much lower concentrations are employed. There is no upper limit in concentration but amounts over 5% by weight offer no particular advantage and are not justified economically.

The stabilizers may be added not only at the beginning of an operation, but they also may advantageously be added periodically or continuously during the course of a run. Depending upon the particular operating conditions, upon the type of substance being treated, and/or upon the kind of painting to which a phosphatized article may later be subjected, the presence of excess nitro aromatic stabilizer may occasionally cause staining of the work, or crystallization of the excess stabilizer within the apparatus, and/or a phenomenon whereby the treated article appears to be "smoking" (i.e., giving off fumes) as it is withdrawn from the phosphatizing bath. One of the main advantages of using combinations of several nitro aromatic compounds simultaneously is that this technique helps to minimize or overcome the foregoing difficulties. Picric acid in particular is a highly effective stabilizer. In fact, it can be used effectively at concentrations as low as 0.001% by weight. In certain applications, however, it tends to cause staining of the "work." In instances where objectionable staining is being encountered, this can be overcome by using relatively small amounts of picric acid in combination with one or more other nitro aromatic stabilizers, and/or by replenishing the supply of stabilizers perodically during a run, so as to avoid the presence of too much nitro aromatic stabilizer at any given moment.

The term "chlorohydrocarbon solvent" as used herein is intended to refer primarily to chloro substituted hydrocarbon solvents having from one to about three carbon atoms including materials such as methylene chloride, methyl chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, and the like. Of these compounds, the chlorohydrocarbon solvents containing two carbon atoms are preferred; and trichloroethylene and perchloroethylene are particularly preferred. However, the present invention is also to be understood as being applicable to the stabilization of fluoro and fluoro-chloro substituted hydrocarbon solvents as well.

A better understanding of the invention will be gained from the following working examples.

Example 1

An accelerated laboratory test was devised to simulate the stabilizing action of various agents of the invention in an actual anhydrous trichloroethylene phosphatizing bath operated at reflux conditions for applying a phosphate coating on metallic surfaces. The base bath composition for this test consisted of 94.5% by weight trichloroethylene, 0.5% by weight phosphoric acid, and 5.0% by weight amyl alcohol as a phosphoric acid solubilizing agent. The trichloroethylene used for the runs reported was a technical grade containing 0.01% by weight pentaphen (p-tertiary amyl phenol) and 0.3%) by weight diisobutylene as an oxidation stabilizing system. The test was carried out as follows:

To 500 ml. of bath, maintained at the reflux temperature of the trichloroethylene, 0.1 g. of high purity zinc dust was added for a period of 10 minutes. After this interval, the bath was filtered for the removal of the zinc dust and 100 ml. of the bath was separated from the filtrate and mixed thoroughly with an equal volume of water in a separatory funnel. The water layer was then decanted from the liquid mixture and analyzed for water soluble chlorides. The measured result of the test is the amount of chlorides present which is considered to vary proportionately with the degree of trichloroethylene decomposition and corrosivity potential resulting therefrom.

The following table shows the amount of chlorides found for runs made in accordance with the test proce-

dure for a phosphatizing bath with and without the stabilizing agents of the invention.

TABLE I

Run No.	Stabilizing Agent	Conc. by Wt. Percent	P.p.m. Chlorides
1	None		50.
2	Nitrobenzene	0.5	1.
3	m-Dinitrobenzene	0.1	Less than 1.
4	o-Nitrotoluene	0.5	3.
5	m-Nitrotoluene	0.4	Less than 1.
6	o-Nitroethylbenzene	0.5	4.
7	o-Nitroisobutylbenzene	0.5	Less than 1.
8	o-nitroanisole	0.4	Do.
9	p-Nitroanisole	0.4	2.
10	2-nitro-4-aminoanisole	0.5	Less than 1.
11	3-nitro-5-aminoanisole	0.5	Do.
12	o-Nitrochlorobenzene	0.4	Do.
13	p-Nitrophenol	0.4	Do.
14	o-Nitrophenol	0.4	Do.
15	2,4-dinitrophenol	0.4	Do.
16	p-Nitrobenzoic acid	0.4	Do.
17	3,5-dinitrobenzoic acid	0.4	Do.
18	2,4-dinitrotoluene	0.1	Do.
19	4-nitrotoluene-2 sulfonic acid	0.4	Do.
20	3-Nitrophthalic anhydride	0.5	Do.
21	o-Nitrobiphenyl	0.5	3.
22	9-nitroanthracene	0.5	5.
23	1-nitronaphthalene	0.5	4.
24	2-nitrobenzamide	0.5	Less than 1.
25	p-Nitrophenylhydrazine	0.5	7.
26	Picrolonic acid	0.4	Less than 1.
27	p-Nitrophenylacetonitrile	0.4	Do.
28	m-nitrobenzyl alcohol	0.4	Do.
29	5-nitroquinoline	0.1	Do.
30	3-nitrodibenzofuran	0.4	3.

It will be obvious from the above results that the stabilizing compounds of the invention are significantly effective in inhibiting the formation of corrosive chlorides. To determine what correlation exists between the different levels in chloride formation obtained in the above test for the stabilized and unstabilized baths with actual corrosion, the base phosphatizing bath composition and the phosphatizing bath composition containing m-dinitrobenzene as reported in Run 3 above where run in separate alloy steel vessels side by side under identical conditions operated at reflux temperature and in contact with iron powder. The operation was continued for a period of three weeks. After this interval of operation corrosion was very evident in the vessel containing the base phosphatizing composition without a stabilizing agent of the invention, exhibiting approximately a 1/16 inch accumulation of salts at the condensate region of the vessel, while corrosion in the vessel containing the phosphatizing composition of Run 3 was barely, if at all, detectable. Moreover, in the above reported runs, it was noted that the stabilizing compounds of the invention in general effectively improved the coating weights of phosphate on the workpiece. This feature, of course, provides a further significant commercial advantage since it enables shorter immersion times in the phosphatizing bath to obtain a desired thickness of phosphate coating.

Example 2

The test of Example 1 was repeated with the phosphatizing bath of that example in which perchloroethylene containing a conventional oxidation stabilizing system was employed as the chlorohydrocarbon solvent in place of trichloroethylene in the same amounts. A run was conducted with such a phosphatizing bath without a stabilizing agent of the invention and the amount of chlorides was determined to be 50 p.p.m. or comparable to the result obtained when trichloroethylene was employed in the bath unstabilized. Another run was conducted with the same base phosphatizing bath under identical conditions but containing 0.4% by weight 2,4-dinitrotoluene and the amount of chlorides was determined to be 2 p.p.m. which is obviously a significant reduction from the 50 p.p.m. level observed for the base phosphatizing bath.

Example 3

The test of Example 1 was repeated with the phosphatizing bath of that example in which a commercial grade methyl chloroform containing a conventional oxidation stabilizing system was employed as the chlorohydrocarbon solvent in place of trichloroethylene in the same amounts. A run was conducted with such a phosphatizing bath without a stabilizing agent of the invention and the amount of chlorides was determined to be 100 p.p.m. A second run was conducted with the same phosphatizing bath under identical conditions but containing 0.4% by weight 2,4-dinitrotoluene and the amount of chlorides was found to have been reduced to 3 p.p.m.

Example 4

A further test was devised to simulate the stabilizing action of agents of the invention in acid conditions which might be expected to develop in a chlorohydrocarbon solvent in use over an extended period of time. The base composition for this test consisted of 500 ml. of an unstabilized trichloroethylene containing 4.5% by wt. amyl alcohol which is acidified by adding thereto ½% by wt. acetic acid and 0.5 gram water. An alcohol is included with the chlorohydrocarbon solvent in this test since the presence of alcohol has utility in certain applications employing chlorohydrocarbons and such combination therefore may be very desirable as a product sold in commerce. The presence of alcohol in a chlorohydrocarbon solvent has been found to actually promote acid conditions so that the stabilizing action of the agents of the invention is more critical in such combination than in the chlorohydrocarbon solvent alone. The acid containing base composition was run in accordance with the test of Example 1 for the determination of chloride formation and the amount of chlorides was found to be 50 parts per million.

To the same acid-containing base composition, 0.4% by weight 2,4-dinitrotoluene was added and the test of Example 1 repeated. The amount of chloride formed was found to be only one part per million, demonstrating the effective stabilizing action of the agents of the invention under such conditions.

The unstabilized trichloroethylene of the base composition was replaced with a like amount of a technical grade trichloroethylene containing 0.01% by weight pentaphen and 0.3% by weight diisobutylene as an oxidation stabilizing system and a further run was made in accordance with the test of Example 1. The amount of chlorides was determined to be 50 parts per million. This result is the same as the result with the acid composition containing unstabilized trichloroethylene and shows that the conventional oxidation stabilizing system had no material effect in inhibiting the progressive deterioration of a chlorohydrocarbon due to acid conditions.

To the acid composition containing technical grade trichloroethylene above, 0.4% by weight 2,4-dinitrotoluene was added and the test of Example 1 was repeated. The amount of chlorides was found to be one part per million indicating that the agents of the invention offer the same effectiveness in stabilizing action under acid conditions in the presence or absence of a conventional oxidation stabilizing system and consequently are not dependent on but compatible with such an additional system.

Example 5

A standard stability test was conducted to demonstrate the further stabilizing action of the agents of the invention to prevent oxidative decomposition under conditions of heat, light, and oxygen simulating use conditions. The extent of decomposition is measured in terms of acidity, corrosive chlorides, and high boiling polymeric decomposition products formed during the test.

In executing the test, a 200 ml. sample of the chlorohydrocarbon solvent to be tested in placed in a flask and is refluxed for 4 hours in the presence of iron powder during which time the condensed vapors are continuously

recycled through a water layer. Concurrently, the boiling sample is irradiated with ultraviolet light and oxygen gas is bubbled therethrough.

At the end of the reflux period the acidity of the water layer is measured and reported as ml. of 1.0 N HCl.

A sample of the chlorohydrocarbon solvent is then removed from the flask, filtered, and mixed thoroughly with an equal volume of water in a separatory funnel. The water layer is separated and analyzed for water-soluble chlorides. The amount of chlorides present in parts per million of chlorides is reported.

A separate sample of the chlorohydrocarbon solvent is removed from the flask and submitted to gas chromotography which is a useful technique for separating the high boiling decomposition products formed during the test. By this technique the relative amounts of such decomposition products formed betwen various runs can be measured. In this determination, a 0.01 ml. sample is injected into a Perkin-Elmer model 159–B vapor fractometer fitted with a 4 meter "K" column employing "Carbowax" 1500 polyethylene glycol as a partitioning agent. The determination is carried out at a temperature of 190° C. The elution tracing which is obtained shows two bands characteristic of the oxidation or decomposition products of the chlorohydrocarbon. The area under these curves is approximated and this figure is reported as a measure of the relative amount of decomposition products present.

An unstabilized trichloroethylene with and without a stabilizing agent of the invention was run in accordance with the foregoing test procedure. A comparison of the results on the various determinations for these runs is reported in the table below:

TABLE II

Run	Composition	Acidity as 1 N HCl	P.p.m. Chlorides	Rel. Amt. Decomposition Products
1	Unstabilized trichloroethylene.	0.46	25	48
2	Unstabilized trichloroethylene+0.4 wt. percent 2,4-dinitrotoluene.	0.36	3	0

It will be seen from the above results that the stabilizing agent of the invention is effective in inhibiting the oxidation decomposition of a chlorohydrocarbon solvent. It is to be noted, in particular, that with the addition of the stabilizing agent the formation of high boiling oxidative decomposition products was prevented.

Example 6

The standard stability test of Example 5 was repeated in runs with an unstabilized trichloroethylene containing 5% by wt. amyl alcohol with and without a stabilizing agent of the invention. A comparison of the results is reported in the following table:

TABLE III

Run	Composition	Acidity as 1 N HCl	P.p.m. Chlorides	Rel. Amt. Decomposition Products
1	Unstabilized trichloroethylene+5 wt. percent amyl alcohol.	2.32	100	40
2	Unstabilized trichloroethylene+5 wt. percent amyl alcohol+0.4 wt. percent 2,4-dinitrotoluene.	0.44	3	0

It will be obvious in comparing the results of Run 1 above with the results of Run 1 in Example 5, that the addition of the alcohol promotes the decomposition of a chlorohydrocarbon solvent, particularly by increasing acidity and chloride formation.

It will be noted, however, by comparing Run 2 of Example 6 with Run 2 of Example 5 of the invention that the stabilizing agent of the invention is nearly equally effective in inhibiting the decomposition of the chlorohydrocarbon in the presence of an alcohol, particularly in preventing the formation of high boiling oxidative decomposition products. Through the use of the stabilizing agents of the invention, therefore, a chlorohydrocarbon solvent and an alcohol may be compounded together as a product of commerce for various end uses where such a combination is desirable without the risk of causing increased product deterioration.

Example 7

While the reduction of chloride ion concentration is a good indication of the prevention of trichlorethylene breakdown, it is also desirable to demonstrate that under practical conditions the phosphatizing solutions of this invention are substantially non-corrosive. For this purpose, a demonstration was set up according to the following procedure. A glass kettle, having a capacity of 3 liters, was equipped with glass cooling coils located on the inside of the kettle near the top, an air vent, a stopper, and a stainless steel coil projecting through the stopper and into the area of vapor level of the trichloroethylene phosphatizing composition. A heating mantle was provided around the bottom half of the kettle to maintain the kettle at the reflux temperature of the solution.

The vessel was charged with 1500 cc. of technical grade trichlorethylene containing .3% diisobutylene and 0.01% pentaphen as oxidative stabilizers, 5.0% n-amyl alcohol, and 0.5% commercial 85% orthophosphoric acid.

The stainless steel coil was composed of No. 316 stainless steel and was carefully weighed. Cooling water was run through the glass condenser coil as well as through the stainless steel condenser coil. When the solution was brought to reflux, the stainless steel coil functioned in the same manner as a cooling coil in a commercial unit. The stainless steel coil was removed at the end of 186 hours and weighed. The corrosion rate is reported in terms of mils per year of stainless steel which is corroded away.

In order to make this test typical of actual practice, iron powder was added each day to simulate work load. The phosphoric acid reacts with the metal surface to form iron phosphate with the liberation of hydrogen. Thus, phosphoric acid is consumed in relation to the square feet of metal surface introduced into the bath. Calculations from commercial units have shown that 17 sq. ft. of work require about 2 cc. of phosphoric acid. In the laboratory, it was found that 1 g. of iron powder (high purity) required about 2 cc. of phosphoric acid. Thus, iron powder has been used in the laboratory to simulate commercial runs. In the present study, 1.5 g. of iron powder was added each day to correspond to a work load of 64 sq. ft. per gal. of bath per day. This level of work load is commensurate with that found in the industry.

When this corrosion test was run in the absence of any of the nitro aromatic stabilizers of the present invention, the corrosion rate exceeded 500 mils of stainless steel per year.

In the following examples, i.e., Examples 8 through 13, corrosion tests were run in accordance with the test procedure of Example 7. Various amounts of nitro aromatic stabilizers were added to the initial charge of technical grade trichlorethylene; and daily additions of certain stabilizers were also made. The daily additions always included the iron powder and also p-benzoquinone, the latter being added at the rate or from 10 to 23 grams per 1000 square feet of work load. Furthermore, the daily additions usually included one of the

nitro aromatic stabilizers, the amounts thereof being reported.

Example 8

Following the test procedure of Example 7, there was added to the initial charge of trichlorethylene 0.4% by weight of dinitrocumene. The daily additions included the quinone compound, but no nitro aromatic compound. The corrosion rate observed at the end of 186 hours was 15 mils of stainless steel per year.

Example 9

To the initial charge of trichlorethylene there was added 0.4% by weight of a commercially available mixture of isomers of dinitrotoluene. The daily additions included (in addition to the quinone compound) further amounts of dinitrotoluene, at the rate of 45 grams per 1000 square feet of work load. The observed corrosion rate was 4 mils per year.

Example 10

To the initial charge of trichlorethylene, there was added 0.4% by weight of dinitrobenzoic acid. The daily additions included picric acid, at the rate of 3 grams per 1000 square feet of work load. The observed corrosion rate was 9 mils per year.

Example 11

To the initial charge of trichlorethylene, there was added 0.4% by weight of dinitrotoluene. The daily additions included picric acid. at the rate of 3 grams per 1000 square feet of work load. The observed corrosion rate was only 1 mil per year.

Example 12

To the initial charge of trichlorethylene, there was added 0.2% by weight of dinitrocumene, 0.2% by weight of dinitrobenzoic acid, and 0.005% by weight of p-benzoquinone. The daily additions included picric acid, at the rate of 2 grams per 1000 square feet of work load. The observed corrosion rate was 16 mils per year.

Example 13

To the initial charge of trichlorethylene, there was added 0.2% by weight of dinitrotoluene and 0.2% by weight of dinitrobenzoic acid. The daily additions included picric acid, at the rate of 2 grams per 1000 square feet of work load. The observed corrosion rate was 3 mils per year.

Example 14

A phosphatizing operation was carried out in which metal furniture parts were phosphatized, using apparatus which was essentially similar to a dip-type commercial degreaser unit. The unit was charged with a solution containing 5% by weight of pentanol-1, 0.4% by weight of 85% phosphoric acid, 0.4% by weight of dinitrotoluene and the remainder trichlorethylene which contained small amounts of the commercially used stabilizers, pentaphen and diisobutylene. This solution was heated to boiling; and the metal parts were suspended on a monorail conveyor, passed down through the trichlorethylene vapor zone, dipped in the phosphatizing solution, and then passed up through the trichlorethylene vapor zone. The articles were subsequently painted, using a standard paint, "Dulux" beige, enamel No. 752–66295. This operation continued over a period of weeks, with periodic additions of solvents to maintain the bath level, together with small amounts of p-benzoquinone and amounts of dinitrotoluene sufficient to maintain the approximate initial concentration. Representative samples of the painted parts, when subjected to a standard salt spray test, performed at least ten times as well as painted samples prepared in the same way from unphosphatized parts.

The foregoing examples demonstrate the superior corrosion results obtained when using the nitro aromatic stabilizers of the present invention. The polynitro aromatic stabilizers, especially when two or three of them are used simultaneously, give particularly good results.

When supplying solvent for use in a number of different phosphatizing baths which may be operating at widely differing rates of work throughput, it is most desirable to be able to supply a composition comprising the chlorohydrocarbon solvent plus the oxygen-containing solvent plus the nitro aromatic stabilizer, but not containing any phosphoric acid. This composition can be used to replenish depleted phosphatizing baths, with the phosphoric acid being added separately in whatever amount is needed to maintain the desired strength in the bath. The reason this is desirable is that the factors determining the consumption of phosphoric acid often differ from the factors determining solvent consumption. Phosphoric acid consumption is largely influenced by the area of the work treated and the thickness of the phosphate coating to be applied. Solvent consumption is largely influenced by the amount of heat applied and by the efficiency of the apparatus in preventing loss of solvent vapor. Physical drag-out, of course, leads to consumption of both phosphoric acid and solvent.

In practice, it frequently happens that one of the two solvent components tends to be used up somewhat more rapidly than the other. In the case of trichlorethylene on the one hand and a C–4 or C–5 alcohol on the other hand, the alcohol is generally used up somewhat more rapidly. It has been found, for instance, that in order to keep a phosphatizing bath operating with from 1% to 10% of the alcohol in the bath, it is very helpful to make available a solvent composition containing from 10% to 40% of the oxygen-containing solvent, such as the alcohol. Furthermore, it is frequently advantageous for such compositions to contain much larger amounts of the nitro aromatic stabilizer constituent than are employed in the actual phosphatizing baths. For example, amounts of stabilizer in the range of 1% to 5% by weight are particularly useful. If these alcohol-rich compositions were to be used, along with added phosphoric acid, as the entire bath, the results obtained would not be good, because the large amount of alcohol slows up the coating rate and may even completely prevent any phosphatizing. But when the alcohol-rich compositions are added in relatively smaller proportions, along with phosphoric acid, to baths which have become depleted, very desirable long-term operating results are obtained. The chlorohydrocarbon content of such compositions accordingly will vary from about 99% to about 60% by weight of the entire composition; the oxygen-containing solvent will account for from about 1% to about 40% by weight of the composition; and the combination of the chlorohydrocarbon constituent plus the oxygen-containing solvent constituent plus the nitro aromatic compound constituent will amount to at least 98% by weight of the total composition.

It is to be understood that various modifications of the present invention will occur to those skilled in the art upon a reading of the foregoing description. All such modifications are intended to be included as falling within the scope and spirit of the present invention as may be reasonably covered by the following claims.

We claim:

1. A chlorohydrocarbon solvent composition consisting essentially of from about 99% to about 60% by weight of a chlorohydrocarbon selected from the group consisting of trichloroethylene and perchloroethylene; from about 1% to about 40% by weight of at least one oxygen-containing solvent from the group consisting of alcohols containing from 3 to 8 carbon atoms and acid phosphate esters derived by reacting phosphoric acid with such alcohols; and a stabilizing amount of at least one nitro aromatic compound, which compound contains at least two nitro groups of the type which are bonded directly to an aro-

matic nucleus; the sum of the foregoing constituents amounting to at least 98% by weight of the total composition.

2. A composition according to claim 1 in which the said oxygen-containing solvent is an alcohol containing from 3 to 8 carbon atoms.

3. A composition according to claim 1 in which the said oxygen-containing solvent is an alcohol containing four carbon atoms.

4. A composition according to claim 1 in which the said oxygen-containing solvent is an alcohol containing five carbon atoms.

5. A composition according to claim 1 in which the said oxygen-containing solvent is a mixture of an alcohol containing from 3 to 8 carbon atoms and an acid phosphate ester derived by reacting phosphoric acid with said alcohol.

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LEON ZITVER, *Primary Examiner.*

DANIEL D. HORWITZ, *Examiner.*