United States Patent Office 2,820,016 Patented Jan. 14, 1958

2,820,016

CORROSION INHIBITING COMPOSITION AND INDICATOR THEREFOR

Philip J. Raifsnider, Richmond, and Rita Wieland, Berkeley, Calif., assignors to Shell Development Company, New York, N. Y., a corporation of Delaware

No Drawing. Application June 30, 1954 Serial No. 440,524

5 Claims. (Cl. 252—408)

The present invention relates to improvements in the prevention of corrosion of metal surfaces which normally occurs in the presence of air and water vapor or aqueous condensates. More particularly, this invention pertains to a novel means for following the depletion of a nitrite, which provides vapor phase inhibition, to determine the point at which the inhibitor should be renewed.

Partially enclosed or completely enclosed metal-containing objects are usually housed, packaged, enveloped, or placed in a container under such conditions or by means of such an enclosing material that moisture and air are either present at the outset or may enter through the container walls, thereby causing corrosion. For example, although various machined metal parts are usually packaged in waxed or oiled paper or in other materials which, in fact, are only partially impermeable to water vapor, it has been found necessary also to cost the metal surfaces with a protective coating of oil, grease, or the like, in order to obtain a further degree of corrosion prevention. In many cases, additional corrosion preventive means have been resorted to, such as the use within the container or package of a dehydrating agent of the type of silica gel or alumina. Even when the container walls are completely impervious to gases or water vapor, corrosion of the metal part will still occur because it is substantially impossible to avoid entry of water vapor at the time when said parts are being placed in the container.

Within recent years an improved means for the storage of corrodible metal articles has been developed, comprising the use of corrosion preventives having low vapor pressure but sufficient to form an atmosphere surrounding the corrodible metal article which prevents or minimizes corrosion. The corrosion preventives having the character just described are referred to hereinafter as "vapor phase corrosion inhibitors." While a number of different classes of materials have been employed for this particular purpose, the present invention contemplates an improvement in the use of vapor phase inhibiting materials wherein an ionizable nitrite salt or constituent is present. This group is exemplified particularly by materials containing or capable of releasing nitrite ions. They have been fully described in a number of patents to Wachter et al., including U. S. 2,643,178; 2,643,177; 2,643,176, and two patents to Hutter, namely U. S. 2,521,311 and U. S. 2,534,201.

The nitrite materials contemplated, or formulations producing nitrite ions, especially are those having a vapor pressure greater than about 0.00002 mm. mercury at 21° C. and preferably are water-soluble substances. They may be organic base nitrites or inorganic nitrites as more particularly defined hereinafter.

One of the shortcomings inherent in the previous use of these materials has been the inability of users to determine the point at which the inhibitor has become depleted to such a point that there is insufficient corrosion protection. The amount of inhibitor is ordinarily so small and the presence of other materials, such as binders and the like, so prevalent that mere inspection of the packages does not provide the necessary information with respect to determining the presence or absence of sufficient corrosion inhibitor. Hence it will be seen that the danger always exists that the inhibitor will be depleted to such an extent that corrosion commences before the article being protected is either put in service or rewrapped for further storage.

It is an object of the present invention to improve the process of using vapor phase corrosion inhibitors. It is another object of this invention to improve the process of utilizing nitrite corrosion inhibitors. It is a further object of this invention to improve vapor phase corrosion inhibiting compositions and fibrous articles of manufacture. It is an additional object of the invention to provide improved vapor phase corrosion inhibitor compositions and products containing ionizable nitrite salts. Other objects will become apparent during the following discussion.

Now, in accordance with this invention, it has been found possible to detect the point at which corrosion protection reaches any arbitrarily established minimum in the system described above, by applying to a solid sheet material, originally coated with a vapor phase corrosion-inhibiting proportion of an ionizable nitrite salt, a small amount of an aqueous solution of a reduced redox dye having a negative redox potential, at pH 7, said aqueous solution being modified by the presence of a water-miscible organic liquid having a higher solvent capacity for the nitrite than water and substantially chemically inert towards the nitrite, dye and reducing agent. When the paper still contains at least about 0.1 gram per square foot of a nitrite, the dye is immediately converted (oxidized) to a different (usually intense) colored form. If the amount of nitrite is lower than this limit, the solution remains substantially colorless (or of a clearly observable different color).

Still in accordance with this invention, improved operation of the process is obtained by using a special class or classes of reducing agents in converting and maintaining the dye in its colorless or light colored form. This preferably comprises α-ketocarboxylic acids and sodium formaldehyde sulfoxalate in a weight proportion between 16 and about 1. The presence of the former stabilizes the solution against inadvertent reversion of the dye to the oxidized state, while the latter converts the dye to the reduced state more rapidly and results in a solution having less color in that state than if the former were used alone. More stable (but slightly colored) solutions are obtained by using reducing acids (such as ascorbic acid) as the sole reducing agent.

Again in accordance with this invention, the solution preferably comprises the following ingredients in the stated proportions:

	Percent
Water	50–85
Water-miscible organic solvent	10–40
Redox dye	0.02– 1
Reducing agent	0.5 –10

This solution is acidified to below pH 5 either by the acidity of one or more of the essential components or by means of an added acid, preferably a strong mineral acid. The amount of reducing agent is sufficient to convert the dye to the reduced state, and the weight ratio of water to organic liquid preferably is within the range from about 2:1 to about 5:1.

In practice, vapor phase corrosion inhibitors are employed under two principal sets of circumstances. These comprise first the coating or impregnation of the inhibitor

on a wrapping material, such as paper or the like, in which the metal article is to be confined or wrapped. Secondly, the inhibitor may be utilized as a powder distributed upon the surface of a metal article, for example, the interior surfaces of a motor or the like. The present invention applies especially to the first set of circumstances wherein the vapor phase inhibitor is coated upon a paper or other similar base material but also may be utilized by applying the indicator solution to a powder (dusted on any solid surface) to determine the virtual presence or absence of nitrite ions.

The class of redox dyes suitable for the present purpose includes especially those having a redox potential less than about 0.1 volt at pH 7, measured at 30° C. Preferably the redox dye has a negative redox potential. The principal groups of dyes included within this definition include particularly the indigo sulfonic acid salts, oxazolines, thioxenes, and azines.

The indigo sulfonic acid derivatives particularly suitable for the present process include particularly the alkali metal (sodium or potassium) salts of indigo mono-, di-, tri-, and tetra-sulfonic acids. A typical member of this group includes 5,5'-indigo disulfonic acid disodium salt. Oxazines and thioxenes which are suitable for the present purpose include the most favorable indicator, namely, methylene blue. In addition other members of this group include Lauth's violet, nile-blue, brilliant cresol blue, methyl Capri blue, and ethyl Capri blue. Other materials of this class include fast cotton blue and muscarim as well as gallocyanin and brilliant alizarin blue.

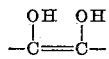
Azines include the safranines such as phenosafranine, dimethyl phenosafranine, tetramethyl phenosafranine, tetraethyl phenosafranine, safranine-T and safranine blue. The rosindulines and their derivatives may be employed, such as isorosinduline No. 1, No. 2, and No. 3, as well as induline scarlet, sulfonated rosindone and rosinduline 2G. Another type of azine suitable for the present purpose is represented by neutral red.

The above types of indicators in their oxidized states are highly colored materials, use of which is made in the subject process. In their reduced state (as applied to the vapor phase inhibitor) they are colorless or substantially so, possibly containing a yellow or yellow-green coloration or much fainter color than when in the oxidized state. As stated hereinbefore, the solutions are to be contained in an acidified mixture of water and water-miscible organic solvent for the subject redox dyes, the solution having a pH below about 5 and preferably between about 2 and 5; together with sufficient reducing agent to reduce the indicator to its substantially colorless (or light colored) form and to just maintain it in that state while being held for use.

The redox dyes defined above are to be utilized in their leuco or reduced form. If they are more readily available in the oxidized state, they may be reduced by the use of a wide variety of reducing agents. These may include strong reductants such as titanous or chromous chlorides and the alkali metal salts (especially sodium salts) of aldehydes, or their derivatives such as sodium formaldehyde sulfoxalate.

These may be hydroxyalkyl sulfoxalates prepared by the reaction of an alkali metal hyposulfite with aldehydes and ketones, particularly formaldehyde or hydroxy aldehydes such as glucose.

The preferred class of highly stable reducing agents comprise especially the carbohydrate (preferably monosaccharide) acids and more particularly those carbohydrate acids containing an unsaturated carbon-to-carbon linkage, especially where the carbon atoms so linked have directly attached hydroxyl groups. The most effective stabilizing derivatives of this kind contain the grouping



It will be understood that in the class of acids referred to herewith are included the lactones (inner esters) directly derived therefrom. While the most effective member of this class is ascorbic acid, other acids of the general class of polyhydroxy alpha ketocarboxylic acids, preferably alpha keto β-hydroxy carboxylic acids (or alpha-hydroxy - beta-keto) and alpha-keto β,γ-dihydroxy carboxylic acids (including lactone form and enol-lactone form) are suitable. If the essential ingredients are not acidic enough to produce an indicator solution having a pH below 5, supplementary acids are incorporated. Acids which may be used in producing the desired low pH include particularly sulfuric, phosphoric and hydrochloric acids. Hydrochloric is preferred. Organic acids, e. g. water soluble carboxylic acids (acetic, etc.), may be used. However, carbohydrate acids such as ascorbic acid not only act as the reducing agent for the redox dye, but provide the required degree of acidity as well.

The chief object in employing a mixture of water with a water-miscible organic solvent for the redox dye is to produce the maximum speed of color indication coupled together with a proper drop shape for determination of an accurate color reaction. If water is used as the sole solvent the reaction with the nitrite on the paper surface is relatively slow and may at times result in an indefinite determination of the color change. This is due to the fact that most of the vapor phase inhibitors containing or producing nitrite ions or radicals have only a limited solubility in water. On the other hand, if organic solvents having increased solubility both for the dye and for the nitrites are employed as the only solvent in the absence of water, poor drop formation occurs when the solution is placed on the paper or equivalent surface. Due apparently to the reduced surface tension of such solutions, the drop spreads in all directions resulting in an extremely small amount of the solution contacting a given area of the paper or other support.

Since the object is to gain an immediate reaction with a limited portion of the vapor phase inhibiting surface, it has been found that improved test results are obtained by the mixture of water with water-miscible organic solvents in the ranges stated hereinbefore, namely between 50 and 85% of water combined with between about 10 and 40% by weight of the solvent. Preferably, the ratio of water to organic solvent is between about 2:1 and about 5:1 by weight. Suitable solvents include especially polar aliphatic organic liquids such as water-miscible alcohols and particularly the lower aliphatic alcohols including methanol, ethanol, propanol and glycol. Ketones may be employed such as acetone, methyl isopropyl ketone and methyl isobutyl ketone, as well as other water-miscible aliphatic ketones. Aldehydes are preferably avoided since they tend to enter into oxidation-reduction reactions and it is desired that the water-miscible organic solvent be substantially inactive chemically toward the remaining ingredients in the solution.

It has been found that the carbohydrate acids defined hereinbefore are capable of being employed as the sole reducing agent but when so utilized they do not completely decolorize the solution of the redox dyes. Moreover, the reduction occurs at a relatively slow rate but the reduced state remains even after long storage of the solutions. Combination of this stable type of reducing agent with other types of reducing agents, e. g. sulfoxalates, enables the reduction of the dye with maximum rapidity and at the same time to a state of less color than is possible when using the carbohydrate acid alone. In storage of the indicator solutions, it is preferred that the solution be prepared as follows:

If used, the reducing agent capable of rapid and more complete decolorization of the dye solution is dissolved in water or in the water-miscible organic solvent or in both and stored separately from a solution of the remaining indicator ingredients. Not more than about one month previous to utilization of the solution the two solutions may be combined and will remain stable for

a period up to about one month and possibly even longer. If at any time during this storage or utilization period the indicator solution gradually assumes the oxidized color state this may be reverted to the reduced state by addition of further quantities of the reducing agent.

The process of this invention comprises application of the indicator solution to a paper (or other support or surface) previously coated or dusted with a vapor phase inhibitor such as those detailed hereinafter. Normally this will occur after this protective paper has been utilized for the purpose of preventing rust or other types of corrosion when wrapped around metallic parts or other metallic surfaces. Such papers normally contain sufficient vapor phase inhibitor to protect the metallic articles against corrosion for a period upwards of about six months to one year or even longer. This normally requires the presence of between about 0.1 and about 3 grams of the nitrite materials detailed hereinafter per square foot of the wrapping surface. The present indicator solutions are designed to indicate the point at which the papers contain the minimum amount of nitrite material which will protect the metallic particles against corrosion. This color change is established arbitrarily, dependent upon the temperature, humidity, value of the metallic articles and other variables, but normally will be at between about preferably 0.1 and 0.2 gram of nitrite material per square foot of the wrapping surface. Thus the indicator solutions will show the oxidized state if placed upon the nitrite-containing wrappers and will exhibit the substantially colorless reduced state if placed upon wrappers containing less than about 0.5 gram (and, more sharply, less than about 0.2) of nitrite per square foot of surface area.

It will be understood that the color change which the redox dye indicator exhibits cannot be clearly defined in words since this will vary widely with the identity of the indicator, the relative amounts of the materials in contact, the pH and temperature of the system, as well as the color of the base materials on which they rest. The preferred means for utilizing the process and composition comprises establishment of the minimum color level to be tolerated (which is arbitrarily set by the factors indicated above), preparation of color standards in the form of spots on paper, such as by printing, or by application of the indicator solution to papers of known nitrite concentration, and comparison of these color standards with the spot produced by applying the indicator solution to the vapor phase inhibitor paper (or other surface) being tested.

The vapor phase inhibitors found to be most effective for use in the present invention comprise water-soluble, organic, or inorganic nitrite compounds having a vapor pressure of at least 0.00002 mm. Hg at 21° C. and forming an atmosphere of nitrite-containing vapors which, upon dispersal in water, yield a solution having a pH value of at least 6. Many of these materials may be employed without further modification but a number of others, as given in detail hereinafter, are improved by the presence of a basic acting agent.

The nitrite substance may be an inorganic nitrite such as ammonium nitrite or a metallic nitrite such as sodium or potassium nitrites, or may comprise an organic base salt of nitrous acid. The organic bases which will form such nitrite salts will usually be amines or nitrogen-containing compounds. Nitrogeneous bases which may be employed in the form of their nitrite salts include aliphatic amines such as isopropyl amine, and diisopropyl amine, urea and thiourea; cycloaliphatic amines, such as cyclohexyl amine; secondary amines such as diisopropyl amine and dicyclohexyl amine, and other amines such as guanidine, piperidine, and morpholine.

If basic acting agents are combined with the nitrite material, it is preferred that the agent have a pH value in excess of 7 when dispersed in water as usually is the case when an inorganic nitrite is used. As stated, the basic agent may be an organic or an inorganic compound. These may be primary, secondary, or tertiary amines, quaternary ammonium bases, or diamides of weak carboxylic (including carbonic) acids which upon hydrolysis yield ammonia (or amines) and the weak acid. Typical basic acting agents useful for combination with the nitrite producing agents are fully described in U. S. patent application of Wachter et al., Serial No. 191,330, filed October 20, 1950, now U. S. Patent No. 2,752,221.

The diamides are preferred and are exemplified by urea and its derivatives, such as dimethyl urea, tertiary amyl urea, reaction products of amines with biuret, and similar substances.

Inorganic salts which are useful as alkaline agents to be combined with the nitrite producing substances are those which hydrolyze in water to give an alkaline reaction to litmus, preferably salts of alkali or alkaline earth metals and a weak acid. These include sodium bicarbonate, sodium carbonate, calcium bicarbonate, borax disodium phosphate, sodium acetate, sodium benzoate, sodium tartrate and similar materials. It is preferred that if a basic acting agent is present, it be utilized in an amount between about 0.05 and about 20 parts by weight for each part of nitrite material. In order to be effective under ordinary storage conditions, it is preferred that the nitrite be present in the confined space in which the metal article is stored in an amount between about 0.1 and about 5 grams of the nitrite compound per square foot of the enclosing surface.

The examples which follow illustrate the use of the process of the present invention and the compositions described hereinbefore.

Example I

The various dye solutions containing the dyes described hereinafter comprised 25 cc. of methyl alcohol, 75 cc. of distilled water, 15 drops of concentrated hydrochloric acid, 8 grams of ascorbic acid, 0.5 gram of sodium formaldehyde sulfoxalate and 0.2 gram of the redox dye. Under these conditions, the indicator solutions were substantially colorless or only contained a tinge of yellow or a related light color. The dyes utilized included neutral red, 5,5'-indigo disulfonic acid disodium salt, and safranine blue.

The indicator solutions were applied in the form of a drop to kraft paper originally containing about one gram per square foot of dicyclohexylammonium nitrite. When the spot of indicator solution was placed upon the freshly prepared paper a brilliant dye color immediately resulted as follows: Neutral red: dark purple color; the indigo dye: blue color; Safranine blue: dark purple color. These papers when aged such as by wrapping metallic articles therein and storing at room temperature for periods up to about six months were radically different due to the decreased nitrite concentration on the paper. All of the papers after the storage period had nitrite concentrations less than about 0.1 gram per square foot of paper. The colors of the indicator solution when placed thereon were as follows: Neutral red: light orange-pink; the indigo dye: light green; Safranine blue: pale red.

Example II

The course of color formation in the indicator solution was followed with respect to response thereof to papers containing varying quantities of dicycloxyhexylammonium nitrite. Utilizing the same indicator solution described above, but wherein the dye was methylene blue, the following results were obtained:

Grams nitrite per square foot of paper	Indicator color
0.09	Green.
0.18	Blue-green.
0.25	Blue.
0.36	Dark blue.
1.0	Very dark blue.

Example III

The same procedure was followed with an indicator solution containing Neutral Red. The results were as follows:

Grams nitrite per square foot of paper	Indicator color
0.02	Light orange.
0.09	Orange-pink.
0.18	Light pink.
1.0	Purple.

Example IV

Another test utilizing the same procedure was made wherein the indicator solution contained Safranine blue with the following results:

Grams nitrite per square foot of paper	Indicator color
0.02	Light red.
0.09	Slightly darker red.
0.18	Do.
1.0	Purple-red.

We claim as our invention:

1. An indicator solution for the determination of nitrite compounds on papers containing a vapor phase corrosion inhibiting nitrite, comprising the following ingredients in the stated proportions:

	Parts by weight
Water	75
Methyl alcohol	25
Methylene blue	0.2
Sodium formaldehyde sulfoxalate	0.5
Ascorbic acid	8

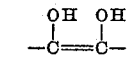
said solution being acidified to a pH value below about 5 with hydrochloric acid.

2. An indicator solution for the determination on nitrite compounds on papers containing a vapor phase corrosion inhibiting nitrite comprising the following ingredients in the stated proportions:

	Percent by weight
Water	50–85
Redox dye	0.02–1
Water-miscible aliphatic polar organic solvent for said dye	10–40
Reducing agent	0.5–10

said dye being in the reduced state said reducing agent being selected from the group consisting of alkali metal aldehyde sulfoxalates, carbohydrate acids containing at least one hydroxyl radical attached directly to an unsaturated carbon atom, and mixtures of the same, wherein the acid: sulfoxalate weight ratio is between about 16:1 and 1:1, the solution being acidified to a pH value lower than about 5, the ratio of water to water-miscible solvent being between about 2:1 and about 5:1 parts by weight.

3. An indicator solution according to claim 2, wherein the reducing agent is a carbohydrate acid containing in its molecular structure the grouping



4. An indicator solution according to claim 3, wherein the carbohydrate acid is an alphaketo acid which contains at least one unsaturated carbon to carbon linkage.

5. An indicator solution for the determination of nitrite compounds on papers containing a vapor phase corrosion inhibiting nitrite, comprising the following ingredients in the stated proportions:

	Percent by weight
Water	50–85
Water-miscible alcohol	10–49
Redox dye	0.05–1
Sodium formaldehyde sulfoxalate and ascorbic acid	0.5–10

said dye being in the reduced state, the ascorbic acid: sulfoxalate weight ratio between about 16:1 and about 1:1, the solution being acidified to a pH below about 5, the ratio being of water and alcohol being between about 2:1 and about 5:1 parts by weight.

References Cited in the file of this patent

"Organic Analytical Reagents" (Welcher), published by D. Van Nostrand Co., New York, page 217.

Acid-Base Indicators, by I. M. Kolthoff et al., The Macmillan Co., New York, 1937, page 162.

The Merck Index, 5th ed., Merck and Co., Inc., Rahway, N. J., 1940, page 15.