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LACQUER AND LIKE COATING COMPOSITION

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This invention relates to improved lacquers and like coating compositions, and more particularly to cellulose ester lacquers, such as nitrocellulose lacquers, which are stabilized against deterioration or discoloration in the presence of metals.

It is well-known that lacquers, and particularly clear or unpigmented lacquers containing a cellulose ester, such as nitrocellulose, dissolved in suitable solvents become discolored upon being stored in metal containers, such as iron or steel drums, or tin or lead lined or plated cans. This discoloration is believed to be caused by the corrosive action of one or more of the ingredients of the lacquer on the metal of the container in which it is stored. Thus, it is believed the discoloration of lacquers under storage conditions is due to contamination by dissolved iron or other metal or by other corrosion products of lacquers upon metals.

It is a primary object of the present invention to prepare a lacquer which is free of the above objection and which, upon being stored in metal containers, does not become discolored or contaminated in such a way as to result in an inferior and commercially undesirable product.

A further object of the invention is to provide a lacquer which is stable and not subject to gelation in the presence of lead containers, lead tubes, lead foil or lead pigments.

Still further objects and advantages of the invention will appear from the following description and appended claims.

The invention is in general carried out and the above objects are obtained by incorporating in the lacquer relatively small amounts of either partially or wholly neutralized oxalic acid or partially or wholly neutralized phosphorus acid, including phosphorus, ortho and pyro phosphoric and alkyl phosphoric acids, the acids being neutralized to the desired extent either by organic amines or by other alkalies or bases capable of yielding salts which are sufficiently soluble in the lacquer composition being treated to obtain the desired results. Organic amines, such as mono and diamyl amine and dibutyl amine are the most suitable bases for the purpose, since they form salts with oxalic and phosphorus acids which are of ample solubility. In general amines of lower molecular weight result in salts of lower solubility, and therefore are less desirable. However, when ethyl phosphoric acids are used, it is even possible to employ caustic soda, as the sodium ethyl phosphate is sufficiently soluble in lacquer for most practical purposes.

A method of stabilizing lacquers and like solutions by incorporating therein small amounts of phosphoric acid or alkali salts thereof, such as various sodium or potassium phosphates, has been described in the patent to C. B. Gilbert No. 2,008,641. However, phosphoric acid has been found to be not nearly as efficient as the organic amine and like salts of oxalic and phosphorus acids which are the subject of this invention. Moreover, the sodium and potassium salts described by Gilbert are not sufficiently soluble in the solvent mixtures generally employed in lacquers to be effective for the intended purpose.

The effectiveness of the salts of the present invention in arresting corrosion, and consequent discoloration, appears to depend on the formation of a thin film of insoluble metal salt, such as iron phosphate, pyrophosphate or the like, on the surface of the metal container. The resulting film, which is closely adherent to the metal surface, tends to stifle any further attack and is so thin as not to affect the original brightness of the metal. It has been found that both the nature of the inhibitor anion and its concentration determine the degree of insolubility of the metal salt formed and possibly also the compactness and adhesion of the salt film, and therefore the effectiveness of inhibition. Moreover, the addition of an organic amine, or other suitable base to the lacquer, serves not only to decrease the acidity of the solution but to increase the concentration of the precipitating anion, thus favoring film formation by increasing the possibility of interaction between the anions and the metal ions and simultaneously decreasing the solubility of the protective salt formed.

The amount of addition agent or inhibitor necessary for best results varies with the inhibitor, with the intensity of corrosion in the absence of inhibitor, and with the composition of the solution being treated. For example, any variation in composition may be expected to change the solubility of the protective salt film and thereby change the concentration of anion necessary for effective and immediate formation of the protective film. As the presence of an excessive amount of water soluble material might be expected to increase the water sensitivity of the dried film solids formed by the lacquer coating, it is in general desirable to use the lowest quantity of inhibitor adequate for continued protection. In the case of nitrocellulose lacquers, for example, from .1 to .2% of the acid, based on the weight of the entire solution, when neutralized with a suitable base to the desired extent, is sufficient to prevent substantially all discoloration or contamination, without detectable effect on the water resistance of the lacquer film. In the case of shellac solutions, however, it is usually necessary to employ larger amounts, e. g. from .7 to .8% of acid based on the weight of the solution, and as shellac is more water sensitive initially than nitrocellulose lacquers, these larger amounts may have a noticeable effect on the tendency of the dried shellac to whiten in water.

The amount of inhibitor necessary also depends on the previous history of the solution to be inhibited. Thus, a solution already badly contaminated with dissolved metal will consume the inhibitor by precipitation and require a correspondingly larger initial quantity. In general, however, it is not practical to use more than about 1% of acid based on the weight of the solution.

The amount of base which should be used to neutralize the acid forming the inhibitor is variable within a rather wide range without affecting seriously the amount of inhibition. Thus it is possible to vary the amount of base from .15 to 1 equivalent of the acid. The most suitable range, however, is from .15 to .6 equivalent, with a preferred ratio of about .3 equivalent. A lower ratio usually results in less inhibition, while higher ratios, especially when a large content of inhibitor is present, results in yellow to brown solutions. Thus, in general, decreasing the acidity of the lacquer solution tends to produce a yellowish coloration, which is irreversible and becomes intensified with time.

A further understanding of the invention will be derived from the following examples of lacquers and like coating compositions, to which small amounts of an inhibitor have been added:

Example I

To a solution of one quarter second nitrocellulose having the composition:

	Per cent
Nitrocellulose	40
Ethyl acetate	21.4
Butyl acetate	21.4
Denatured alcohol	17.2

was added .14% of pyrophosphoric acid and .11% of dibutyl amine, dissolved for convenient mixing in .25% of denatured alcohol. Steel in contact with the above solution remained bright and the solution stayed free from discoloration due to dissolved iron. In the absence of the pyrophosphoric acid-amine solution steel was rapidly attacked by the solution and the solution became brown.

Example II

To a solution of bleached de-waxed shellac in anhydrous denatured alcohol containing 8 pounds of shellac per gallon of alcohol, was added .75% of pyrophosphoric acid and .6% of dibutyl amine, dissolved in .45% of denatured alcohol. Tinned steel in contact with the solution remained bright. In the absence of the inhibitor, however, the solution etched the tin plate rapidly and became discolored.

Example III

To a solution of colorless scrap Celluloid having the composition:

	Per cent
Celluloid	15
Butyl acetate	10
Acetone	20
Methyl ethyl ketone	25
Denatured alcohol	30

was added .1% of pyrophosphoric acid and .08% of mono amyl amine dissolved in .3% of denatured alcohol. The composition, when packaged in lead tubes, remained stable and fluid, whereas in the absence of the pyrophosphoric acid solution gelation occurred in a few hours.

Example IV

To a solution of half second nitrocellulose having the composition:

	Per cent
Nitrocellulose	30
Ethyl acetate	30
Toluene	27
Denatured alcohol	13

was added .2% to 75% phosphoric acid and .07% of diamylamine. When contacted with steel or imperfectly tinned steel the solution did not discolor and the metal remained bright.

As tin plate in general is corroded by lacquer solutions less rapidly than steel, it is possible to use lower concentrations of inhibitor in solutions stored in tin containers. For example, as little as .015% of phosphoric or pyrophosphoric acid in combination with a suitable amount of organic amine will usually give adequate protection from discoloration. Shellac solutions, however, usually require higher inhibitor concentrations, and also the use of tin or terne plate containers rather than uncoated steel.

Of the acids suitable for the purposes of this invention partially neutralized pyrophosphoric acid is preferred, as it may be employed in somewhat lower concentrations or with more corrosive solutions than is possible in the case of orthophosphoric or ethyl phosphoric acid. Moreover, since pyrophosphoric acid is tetra basic as well as being a stronger acid than orthophosphoric or ethyl phosphoric acid, it is possible to employ a higher number of equivalents of organic amine or other suitable base than is the case with the other phosphoric acids without encountering the undesirable yellow solutions obtained when acidity is too low.

Although pure pyrophosphoric acid is not obtainable commercially, it is possible to use almost as effectively commercial syrupy "tetra phosphoric" acid which has been diluted to a phosphorus pentoxide content of about 79.6%, the theoretical value for pyrophosphoric acid. Contrary to expectation, the salts of pyrophosphoric acid are relatively stable and do not form orthophosphoric acid. Thus, aminated pyrophosphoric acid, even after prolonged heating of a concentrated solution in 95% denatured alcohol, retains its greater effectiveness as compared with similar solutions of orthophosphoric acid.

The partially neutralized acids of the present invention are primarily of value in lacquer solutions as inhibitors of discoloration due to corrosion. Nevertheless, under some circumstances they are also effective in the prevention of gelation. Thus, they tend to prevent gelation caused by contact with lead or lead lined containers, or lead pigments, and have a limited anti-gelling action in the presence of some reactive pigments. The effect on pigmented lacquers is demonstrated in the following example:

Example V

To a grind of 1½ pounds of Chinese blue in 1 gallon of nitrocellulose solution containing 4 ounces of heavy dope nitrocellulose in 1 gallon of a mixed solvent having the composition:

Ethyl acetate	per cent by volume	20
Butyl acetate	per cent	20
Toluene	do	50
Denatured alcohol	do	10

was added .2% pyrophosphoric acid and .15% of dibutyl amine dissolved in .5% denatured alcohol. As compared with the untreated grind, which sets to a gel on aging, the phosphated composition remained capable of flow and was more readily incorporated with a clear lacquer base to produce a pigmented enamel.

Although the invention has been described primarily as applied to nitrocellulose lacquers, it may also be used in connection with other cellulose derivative lacquers, such as ethyl cellulose lacquers, as well as with lacquers or solutions containing natural acidic resins, particularly those soluble in alcohols or mixtures of alcohols with other organic solvents, such as shellac, Manila resin, pontianac resin, kauri resin and other copal resins. Moreover, the invention is also concerned with lacquers or solutions containing mixtures of cellulose derivatives and resins of the above type.

It is to be understood that the invention is not limited in its application to the details described herein, since the invention is capable of other embodiments and of being practiced or carried out in various ways. Also it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation, and it is not intended to limit the invention claimed herein beyond the requirements of the prior art.

What I claim is:

1. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution containing a relatively small amount of an acid of phosphorus which has been at least partially neutralized by an organic amine.

2. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution containing not more than about 1% by weight of an acid of phosphorus which has been at least partially neutralized by an organic amine, said neutralized acid being present in an amount sufficient to stabilize said solution against deterioration or discoloration in the presence of metals.

3. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution containing not more than about 1% of pyrophosphoric acid which has been at least partially neutralized by an organic amine, said neutralized acid being present in an amount sufficent to stabilize said solution against deterioration or discoloration in the presence of metals.

4. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution containing not more than about 1% of orthophosphoric acid which has been at least partially neutralized by an organic amine, said neutralized acid being present in an amount sufficient to stabilize said solution against deterioration or discoloration in the presence of metals.

5. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution containing not more than about 1% of an alkyl phosphoric acid which has been at least partially neutralized by an organic amine, said neutralized acid being present in an amount sufficient to stabilize said solution against deterioration or discoloration in the presence of metals.

6. A nitrocellulose solution comprising nitrocellulose and a solvent therefor, said solution having added thereto about .14% of pyrophosphoric acid and about .11% of dibutyl amine.

7. A celluloid solution comprising colorless celluloid and a solvent therefor, said solution having added thereto about .1% of pyrophosphoric acid and .08% of mono amyl amine.

8. A nitrocellulose solution comprising nitrocellulose and a solvent therefor, said solution having added thereto about .2% of 75% phosphoric acid and .07% of diamylamine.

9. A shellac solution comprising shellac and solvent therefor, said solution having added thereto about .75% of pyrophosphoric acid and .6% of dibutyl amine.

10. A pigmented nitrocellulose solution comprising nitrocellulose, a solvent therefor and Chinese blue, said solution having added thereto about .2% of pyrophosphoric acid and .15% of dibutyl amine.

11. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution having added thereto from .1 to .2% of an acid of phosphorus and from .15 to .6 equivalent of an organic amine.

12. A cellulose ester solution comprising a cellulose ester and a solvent therefor, said solution having added thereto not more than about 1% by weight of an acid of phosphorus which has been reacted with from .15 to 1 equivalent of an organic amine, said reaction product being present in an amount sufficient to stabilize said solution against deterioration or discoloration in the presence of metals.

13. The method of stabilizing a cellulose ester solution against discoloration when contacting metal which comprises incorporating in said solution an acid of phosphorus which has been at least partially neutralized with an organic amine.

14. A resinous solution comprising a natural acidic resin which is soluble in alcohols and in mixtures of alcohols and other organic solvents, and a solvent for said resin, said solution containing a relatively small amount of an acid of phosphorus which has been at least partially neutralized by an organic amine.

15. A lacquer solution comprising a cellulose derivative which is soluble in organic solvents, a natural acidic resin which is soluble in alcohols and in mixtures of alcohols and other organic solvents, and a solvent for said derivative and said resin, said solution containing a relatively small amount of an acid of phosphorus which has been at least partially neutralized by an organic amine, said neutralized acid being present in an amount sufficient to stabilize said solution against deterioration or discoloration in the presence of metals.

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