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COATING COMPOSITIONS

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The present invention relates to improvements in coating compositions. More particularly it relates to coating compositions which are resistant to the greening action likely to occur when the compositions contact metal, particularly copper and alloys containing copper, such as bronze or brass, and to a greening inhibitor for such compositions.

Copper-containing articles such as copper, bronze or brass hardware are frequently coated with a clear lacquer to improve their lustre and prevent tarnishing. Where small articles are to be coated it is economical to dip them into a relatively large body of lacquer. Another way of coating small articles is to spray them under conditions in which the excess lacquer is recovered and reused. In these and other known processes, it happens that a relatively large and valuable quantity of lacquer must be used and repeatedly contacted with the copper-containing articles. Under these circumstances the lacquers are often rendered useless by the development therein of a green or blue-green coloration probably attributable to the formation of copper compounds with the constituents of the lacquer or with decomposition products of the lacquer which are always present in greater or lesser amounts. When a large body of clear hardware lacquer develops this foreign coloration it is of no further use for the purpose and must be discarded.

Heretofore malic acid has been proposed as an anti-greening agent for clear coating compositions to solve the problem described above. When incorporated into the composition in small proportions, malic acid substantially decreases the greening effect. However, malic acid is objectionable in that the coatings produced from compositions containing malic acid tend to "bloom." The malic acid tends to crystallize out of the coating, particularly after extreme variations in atmospheric conditions. This produces the cloudy effect known as "bloom" and in extreme instances a white deposit of malic acid is formed on the surface of the coating.

An object of the present invention is to provide coating compositions which are highly resistant to greening.

A still further object of the invention is to provide such a coating composition which when applied results in a coating substantially free from "bloom."

Other objects of the invention will hereinafter more fully appear.

I have found that alkyl mono-esters of malic acid are excellent greening inhibitors for coating compositions. Examples of alkyl alcohols which may be employed in the production of these esters are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, etc. Preferably I employ monoethyl malate as the greening inhibitor. These esters are compatible with coating compositions of resin or cellulose derivative base and are soluble in the ordinary lacquer solvent mixtures. The esters are generally superior to straight malic acid in imparting greening resistance to the composition and to the coating produced therefrom. While with some coating compositions the greening effect cannot be entirely eliminated, in each instance the greening is inhibited by these esters to a greater extent than where free malic acid is employed in equivalent proportion.

Moreover, the coatings containing these esters are free from any observable tendency to "bloom." Even under accelerated test conditions wherein articles coated with my improved lacquer were submitted to alternate high and low humidities no "bloom" developed. Under similar tests coatings containing malic acid became cloudy and crystals of malic acid deposited on the surface of the coating.

It has previously been proposed to use certain malate esters in connection with the problem of the livering or gelling of pigmented nitrocellulose lacquers. Thus, the patent to Burke, No. 2,026,493, describes incorporating ethyl malate in a bronzing lacquer to prevent gelling. The lacquer described in this patent contains a high percentage of bronzing powder as a pigment and the problem to be solved is said to be to keep the lacquer from becoming solid after the bronze powder is incorporated. This is an entirely different problem than the one solved by the present invention which deals entirely with clear lacquers and preventing the development of an undesirable color in them.

Non-limiting examples of the preparation of the greening inhibitors of the present invention are as follows:

Example 1

An alcoholic solution of monoethyl malate was prepared by boiling under a reflux condenser a mixture of 30 g. malic acid with sufficient denatured alcohol (90%) to make a volume of 100 ml. Heating was continued for about 17½ hours, at which time the ratio of saponification number to acid number had risen to about 2, the theoretical value for the mono ester.

Example 2

Monohexyl malate was prepared by heating hexyl alcohol with malic acid in equimolecular proportions at 130 to 140° C. for one hour, the last half hour of the heating being in the presence of a small amount of phosphoric acid as a catalyst. The product was an oily liquid with an acid number of 256 (theory for mono-hexyl malate 257). For use the ester was cut with its own weight of 95% ethyl alcohol.

According to the present invention an alkyl

monoester of malic acid is added to a clear lacquer of a type suitable for use in coating copper-containing articles. Such lacquers are generally of cellulose ester or ether, or of the resin base type. Cellulose nitrate is the preferred base for the lacquer, however, because of its advantageous properties and availability. Among other cellulose derivatives may be mentioned the acetate, aceto-butyrate, and the ethyl ether. Resins which may be used include both natural and synthetic resins of the types well known in the varnish and lacquer art. Thus, among natural resins are damar, elemi and the like and modified natural resins like ester gum. Synthetic resins such as alkyd and phenol-aldehyde resins, oil modified synthetic resins and many others can be employed. In general the composition of the present invention can be said to comprise a base of clear, film-forming resin or cellulose ester or ether.

As a rule the coating compositions are made up of mixed bases and other added materials like plasticizers. The composition comprises a solvent or mixture of solvents of the usual types.

It will be understood that the invention will be employed only with clear coating compositions in connection with which there is a greening problem and which, furthermore, are benefited by the inclusion of an alkyl mono-ester of malic acid. There are some types of compositions which are so corrosive that even an ester of malic acid will not prevent greening. Most of the coating compositions subject to greening, however, will be found to be substantially improved or cured of this defect by treatment according to my invention.

Non-limiting examples of coating compositions of the present invention are as follows:

EXAMPLE 3

	Per cent
Butyl acetate	30
Pent acetate (commercial amyl acetate)	15
Butyl alcohol	14
Ethyl alcohol	9
Toluol	5
Xylol	5
Damar solution (6 lbs. resin/gal. Solvent A)	15
Rezyl resin solution (oxidizing type (oil modified alkyd resin produced by American Cyanamid & Chemical Corp.); 6 lbs. resin/gal. toluol)	5
Shellac solution (6 lbs. shellac/gal. alcohol)	2
	100

125-centipoises nitrocellulose — 5 oz./gal. of above
6-second nitrocellulose — 1 oz./gal. of above

Solvent A

	Per cent
Ethyl acetate	20
Low boiling petroleum naphtha	30
Ethyl alcohol (SD #1)	50
	100

This lacquer has added thereto 2% by volume of an ethyl alcohol solution containing the equivalent of 25 g. malic acid per 100 ml. solution (30.25 g. mono-ethyl malate per 100 ml. solution).

The lacquer shows excellent anti-greening properties and is not subject to "bloom."

EXAMPLE 4

A hardware lacquer with the composition of Example 3 has added to it 2% (by volume) of the 50% ethyl alcohol solution of mono-hexyl malate (prepared in Example 2), in place of the mono-ethyl malate of Example 3.

The resulting lacquer is free from tendency to green and also is not subject to "bloom."

The other greening inhibitors of the invention can be substituted in place of the ones used in the examples. Various other lacquer formulations can be improved as to resistance to greening by the addition of the inhibitors of the invention. It will be understood that the invention is not limited to the proportions of greening inhibitors set out in the examples but that wide variation is permissible. The proportion will usually be quite small, just sufficient to accomplish the desired result. In most instances it is not desirable to use more than 3 or 4% of the alkyl malate based on the lacquer, and 1% or less will usually be preferred.

In the claims which follow I have used the term "clear" referring to my composition to distinguish it from pigmented compositions. I do not, however, intend to exclude colored compositions where the color is produced by conventional means other than pigments.

The term alkyl monoester of malic acid denotes a mixture of the two isomeric monoesters, obtainable by a non-specific reaction such as is illustrated in Examples 1 and 2.

The invention is to be taken as limited only by the scope of the following claims:

1. The method for making a clear hardware lacquer for use in coating copper-containing metal articles by processes such as dipping in which a body of the lacquer is repeatedly brought into contact with successive articles of said metal whereby said lacquer tends to develop an undesirable green color, which comprises adding to a lacquer, comprising nitrocellulose, monoethyl malate in an amount not over about 4%, based on the lacquer, as a greening inhibitor.

2. A clear hardware lacquer for use in coating copper-containing metal articles by processes such as dipping in which a body of the lacquer is repeatedly brought into contact with successive articles of said metal whereby it tends to acquire an undesirable green color, which lacquer comprises a clear, film-forming base, comprising nitrocellulose, and monoethyl malate in an amount not over about 4%, based on the lacquer, as a greening inhibitor.

3. The method for making a clear hardware lacquer for use in coating copper-containing metal articles by processes such as dipping in which a body of the lacquer is repeatedly brought into contact with successive articles of said metal whereby said lacquer tends to develop an undesirable green color, which comprises adding to the lacquer an alkyl monoester of malic acid, in which the alkyl group contains from 1 to 7 carbon atoms, in an amount not over about 4%, based on the lacquer, as a greening inhibitor.

4. A clear hardware lacquer for use in coating copper-containing metal articles by processes such as dipping in which a body of the lacquer is repeatedly brought into contact with successive articles of said metal whereby it tends to acquire an undesirable green color, which lacquer comprises a clear film-forming base and an alkyl monoester of malic acid, in which the alkyl group contains from 1 to 7 carbon atoms, in an amount not over about 4%, based on the lacquer, as a greening inhibitor.

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