STABILIZED COPPER BRONZE POWDERS
AND METHOD

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This invention relates to an improvement in copper bronze powders whereby coating compositions containing the same may be admixed for longer periods prior to use without deterioration of the fluidity necessary to application. More particularly, this invention relates to a method of treating copper containing bronze powders so as to impart additional stability to said powders when incorporated in solutions of nitrocellulose lacquers for coating purposes.

If copper bronze powders now available as standard articles of commerce are admixed with organic solvent solutions of nitrocellulose lacquers, within a brief time a green coloration develops and shortly thereafter the liquidity of the system is lost and the product undergoes a sol to gel transformation. This phenomenon is peculiarly a characteristic of copper containing bronze powders, but in the case of other bronzing powders, such as aluminum bronzes, the difficulty is not known to exist. The principal object of this invention is, therefore, to provide a copper containing bronze powder characterized by improved stability when in contact with nitrocellulose lacquers in solution. The principal object of this invention can be accomplished at two different time intervals. It has been found preferable to accomplish the object of this invention by a special treatment of the copper containing bronze powder prior to its incorporation in lacquer containing protective and decorative coatings. It is also possible, however, to obtain a similar result by incorporating into the nitrocellulose lacquer solution a quantity of the protective additive prior to incorporating therein the copper bronze powder or within a very brief but reasonable period subsequent to the incorporation of the copper bronze powder in the lacquer solution. Time of addition is not particularly critical. However, as previously indicated, it is preferred that the treatment take place prior to the incorporation of the copper bronze powder into liquid bronzing medium. It may be feasible to incorporate the herein described protective additive during the copper bronze powder manufacturing procedure, by addition at one or more stages in commination of the metal particles as they are transferred from one particle size into comparatively thin lamellar flakes characteristic of the metallic bronzes of commerce. The essential components of this invention comprise a copper bronze containing powder, an organic compound selected from the group consisting of water insoluble long chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms and an auxiliary agent in conjunction with the metallic copper bronze of from about one half percent to about five percent by weight of said bronze powder and at least about five-tenths of a percent but not more than about ten percent by weight of said metallic powder of a water insoluble organic acid.

Ratio of fatty acid to amine may vary within appreciable limits. Where the ratio of acid to amine is within the range of 1:7 to 3:1 the range has been found satisfactory for the purposes of the invention. Preferably, the total amount of organic agent in conjunction with the metallic copper bronze powder has been found to be in excess of one percent but less than eight percent and the range of acid to amine within the ratio of from 1:5 to 2:1. From this range it can be seen that the proportion of rosinamine to fatty acid need not be in stoichiometric equivalents. It is believed that the optimum range is quite close to stoichiometric equivalents, although, this relation has not been established by scientific tests.

Copper containing metal bronze powders for the purposes of this invention are generally prepared by subjecting the desired metal to a preliminary comminuting process to reduce the size of the metal to convenient but relatively large initial particle size. The comminuted metal particles are then placed in a ball mill, stamping mill, or other device together with fatty acid lubricant containing from eight to thirty carbon atoms and the metal powders subject to the internal forces of these mills until reduced to the requisite particle dimension. If it is intended that the final powders be used as non-leaching bronzes, the percentage of fatty acid may be of the order of one half percent but if for lasting quality the percentage by weight of the metal is of the order of 2% to 5%. In certain instances the product is also furnished as a metal paste. It is general practice, in these instances, to add volatile thinner to the extent of 20 to 40 percent to produce metal powder pastes.

In accomplishing the ends of this invention it is unnecessary to alter appreciably the prior art processes for preparation of the metal bronze powder. It is reasonable to assume that little difficulty is to be encountered in inclusion of the additive of this invention during bronze powder manufacturing. There is evidence to indicate preferred results are obtained if the metal powder, per se, is subject to treatment rather than to cause treatment to occur in the lacquer solution upon formulation of bronze coatings.

In initial stages of development of this invention advantages of the additive here disclosed were investigated by adding approximately 50 grams of commercially available copper containing bronze powders (already treated with from one and one half to five percent of fatty acid containing at least 8 carbon atoms) in 150 parts of a standard bronzing lacquer (lacquer made as set out in Example 1). To the thus prepared bronzing powder added exploratory percentages of various agents which were deemed to have potential value in stabilizing the coating composition against changes in its viscosity and to prevent attendant gelation occurring shortly (1—4 days) after mixing of the bronze powder with nitrocellulose lacquer solutions.

Through this series of tests it was found that a generic class of materials commonly described as rosinamines were useful in stabilizing the bronze containing lacquer coating. By the term "rosinamine" as used herein, it is intended to refer to commercially available products in which the parent compound contains from about 85 percent to 97 percent of the primary amino compound derived from rosin. The parent group of compounds includes rosinamine, didehydroaminine, dihydroaminine, and tetrahydroaminine. A series of aging tests has established the parent primary amine compound to be preferred for the purposes of this invention. However, a more comprehensive testing of it and related compounds has also shown it to be within the scope of the invention to use secondary rosinamines which are alkylene oxide condensates of the parent primary rosinamine compound. This is possible when the quantity of the alkylene oxide condensed with the parent primary rosinamine is small. In no case should enough alkylene oxide (ethylene oxide) be condensed with the rosinamine...
to render the so derived secondary rosinamine water soluble, or to interfere with the basic character of rosinamines. Thus, both primary and secondary rosinamines are useful for the purposes of this invention, although as stated previously, primary rosinamines appear to be more effective. The non-substituted primary and secondary rosinamines for the purposes of this invention are characterized by an organic residue of a structure similar to the structure of abietic acid, wherein the carboxyl group of the abietic acid is substituted for with an amino group. While primary amines are preferred, the secondary rosinamines (wherein one of the active hydrogens of the parent amine is replaced by an alkyene oxide condensation) are useful to accomplish a similar result. The amount of ethylene oxide, which can be tolerated in condensation with the primary rosinamine, is insufficient to render the so-formed secondary rosinamines water soluble. To illustrate, the limitation of the term "water soluble" as it applies to these compounds it is as follows: when 11 moles or more of ethylene oxide are condensed with one mole of rosinamine sufficient insolubility is observable in the resultant bronzing lacquer coatings to remove practical value and to eliminate it from consideration for the purposes of this invention. If seven moles of ethylene oxide are condensed per mole of primary rosinamine, there is still some water solubility and the usefulness is appreciably lost for my purpose. However, if the ratio of ethylene oxide to rosinamine is reduced to five moles per mole of rosinamine, the secondary amines resulting are useful and the solubility in water at this range is negligible. The expression "water insoluble rosinamine" has therefore been arbitrarily limited and does not embrace secondary rosinamines containing more than eleven moles of alkyene oxide per mole of rosinamine. While experience has been primarily with ethylene oxide adducts of rosinamine, it is obvious that propylene oxide adducts are also potentially available. It should be pointed out that water solubility, per se, is not known to be a detrimental quality in the present application. Water solubility does provide, however, a convenient means of limiting and defining the scope of rosinamines of secondary nature useful for purposes of the invention with practical accuracy in the hereinafter appended claims.

A review of the prior art which relates to the production of metal pastes, pigments, aluminum bronzes, and copper containing bronze powders establishes that it is customary in the art of manufacture of metal powders for pigment use to employ long chain fatty acids to promote the metal powders that lubricate the metal as it is transformed from the larger particle "shred" state to a fine particle lamellar powder state and to assist in polishing the surface of the fine metal powder particles to obtain optimum brilliance. The prior art discloses a number of fatty acids useful during attainment of metal to a finely powdered lamellar state. Among the organic compounds selected from the group consisting of water insoluble long chain aliphatic and aliphatic hydrocarbon acids, containing from 8 to about 32 carbon atoms reportedly used are sunflower oil acids, ricinoleic acid from castor oil acids), oleic acids, myristic acid, palmitic acid, naphthenic acids, etc., which are characterized by their lubricity, water insolubility and soap forming qualities. In the arts which relate to surface activity, it is generally recognized that surface active qualities of long chain aliphatic acids are of little moment until the fatty acid contains at least 8 carbon atoms in its hydrocarbon chain. Most surface active agents contain from eight to about 32 carbon atoms in their longest hydrocarbon chain. For the purposes of this invention, long chain aliphatic and aliphatic hydrocarbon acids within this range are useful and essential in conjunction with the described rosinamines to accomplish the ends of the invention.

As will be shown in the examples, presence of rosinamine alone, in conjunction with the metallic copper bronze powder appears to hasten gelation when in conjunction with a dispersion of the metal powder in a solution of a nitrocellulose lacquer. It has been observed the presence of water in macroscopic quantities delays gelation of benzoyl-containing lacquers, independent of the treatment or method of treatment as described herein. However, it is known that quite small amounts of water are present in nitrocellulose as shipped commercially for it is wetted down with about 30 percent of ethyl alcohol. The ethyl alcohol in turn contains water. This water is carried into bronzing lacquer formulations. The amount so carried in appears not to interfere with the effectiveness of the treatment herein described.

A host of related amines have been used in comparative manner to the rosinamines herein described. These amines include alpha naphthol amine, paraphenylenediamine, and diphenylguanidine. In each test case the useful life of the completed bronzing lacquer containing the recited amines was seriously diminished.

The following examples, while numerous, are by no means to be construed as exhaustive. They are included to illustrate the best methods of practice of the invention and to make clear, by comparison, limitations upon the invention and to illustrate the difference between what is here accomplished and what has been illustrated in the prior art. It is to be noted in passing that attempts to artificially accelerate the age rate of test samples by exposing them to elevated temperatures were in all cases unsatisfactory. This for the reason that developed fluidity of the nitrocellulose suspending medium allowed rapid settling of the heavier metallic bronze powder into closer proximity of the individual metallic flakes and entrapment of thin films of nitrocellulose lacquer between relatively large active metallic surfaces of the copper bronze powder. These conditions appeared to cause very rapid reaction to take place. Increase reaction rates were observed at temperatures of the order of 125° F. Test results recorded herein were at room temperature and within the range of 65 to 90° F. Parts are by weight unless otherwise identified.

EXAMPLE I

A bronzing lacquer was prepared for standard test use in evaluating copper bronze containing powders by cutting 21 parts by weight of 1/2 second and 38 parts by weight of 1/2 second nitrocellulose RS grade in 65 parts butanol, 170 parts toluene, 105 parts xylene, 30 parts naphtha, 45 parts methyl amyl acetate, 70 parts isopropyl acetate and 70 parts methyl isobutyl ketone. The lacquer solution was further plasticized with 15 parts tricresyl phosphate, 80 parts of a 50% soya bean oil modified glycerol phthalate resin containing 35% xylene, and in addition a product containing 35 parts of maleic modified rosin esterified with glycercine.

EXAMPLE II

(Control)

| Cordova rich gold          | 49  |
| Copper bronze powder      | 7.25|
| Stearic acid              |     |
| Lacquer of Example I      | 150 |

were aged together at room temperature. At the end of 4 days, the previously liquid sample had undergone a sol to gel transformation and discolored to a characteristic copper-green color.

EXAMPLE III

| Cordova rich gold          | 49  |
| Copper bronze powder      | 1.25|
| Rosinamine                | 2.50|
| Lacquer of Example I      | 150 |
were mixed together and aged at room temperature. At the end of 30 days the sample was still useful for paint purposes.

**EXAMPLE IV**

**Part A**

200 parts copper bronze powder were exhaustively extracted in a Soxhlet apparatus for 2 hours with chloroform to remove the stearic acid with which the bronze was known to be treated. The extracted bronze was then treated with 20 parts of rosinamine (Resin Anhydride D) in 20 parts of chloroform. Excess rosinamine was removed by further washing with chloroform. A sample was recovered and dried.

**Part B**

Treated bronze from above 50
Std. lacquer solution 150

were mixed together. Upon overnight age, a solid gel formed. Control: gelled in 4 days. The example illustrates ineffectiveness of rosinamines alone.

**EXAMPLE V**

Copper bronze powder (2½% stearic acid) 25
Acetone 25
Rosinamine 25

were mixed together and after several hours the paste was heated and the acetone driven off by evaporation. The product remaining still containing some acetone was mixed with 150 parts lacquer of Example I. The lacquer-bronze mixture had not changed appreciably in viscosity at the end of 30 days at room temperature and behaved normally upon application as a coating.

**EXAMPLE VI**

The following materials were tested, using 50 parts copper bronze powder, 2.5 parts test material and 150 parts lacquer of Example I. The length of time of stability in each case was recorded as follows:

<table>
<thead>
<tr>
<th>Identification</th>
<th>Material</th>
<th>Shelf Life Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>naphthol</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>naphthalene acid</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>naphthyl amine</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>diphenylcarbazide</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>diphenylamine</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Control (No addition)</td>
<td>15</td>
</tr>
<tr>
<td>k</td>
<td>4/5 Carbon atom primary amine</td>
<td>15</td>
</tr>
</tbody>
</table>

**EXAMPLE VII**

Copper bronze powder 50
Rosinamine 5
Lacquer of Example I 150

After mixing, the test material was found to be stable for 14 days whereas control gelled in 4 days. Note: Copper bronze containing from 1 to 1.5 parts stearic acid per 100 parts bronze as purchased.

**EXAMPLE VIII**

Metal powder (copper bronze) 50
Rosinamine 2
Water 2
Lacquer 150

Test was made to determine treatment effectiveness if water was present in substantial amount. Test material gelled overnight. The test established that water in more than trace amounts cannot be tolerated in the system and precautions should be taken to maintain the bronzing lacquer system as dry as possible. That trace amounts of water can be tolerated appears from the fact that trace amounts of water are present in bronzing lacquer solutions prepared as in Example I.

**EXAMPLE IX**

In a test series, 50 parts of copper bronze powder were treated with 2.5 parts, (a) rosinamine naphthenate, (b) rosinamine laurate, (c) rosinamine stearate, (d) rosinamine olate. The test runs were found to be in good condition after the control sample containing no rosinamine salt had gelled.

**EXAMPLE X**

Another series of rosinamine containing bronzing lacquers were prepared using ethylene oxide adducts of rosinamine. In each test 50 parts copper bronze powder were combined with 2.5 parts of rosinamine-ethylene oxide adduct. In this series, it was determined that the smaller the amount of ethylene oxide resided with rosinamine, the more effective was the adduct in stabilizing the metal containing nitrocellulose solution against gelation. With a molar ratio of 1:1 rosinamine-ethylene oxide adduct added the treated bronze gelled in 28 days, whereas the adduct containing 1 mol rosinamine to 11 mols ethylene oxide gelled in 14 days.

From the behavior of this series, as well as in a comparable series where the rosinamine-fatty acid condensations were of fatty acids containing from 2 to 5 carbon atoms, it was determined that rosinamine adducts useful for the purposes of the invention, again, were preferably limited to those of water-insoluble nature.

The percentage of rosinamine useful for the purposes of the invention was found to be within the range of about 0.5% to not more than about 10% by weight of the copper containing metal powder. While effective at lower percentages, the total length of time before gelation fell off rapidly as the amount of rosinamine present was increased above 10%. This evidence suggests one can use too great an amount of amine in relation to fatty acid lubricant inherently present in bronzes of commerce for test purposes.

In all the examples, unless otherwise noted, it is to be observed that the copper bronze powders used as illustrative contained from 2 to 3% of stearic acid. While it is possible and satisfactory for the purposes of the invention to add the rosinamine solution to the lacquer solutions and to form rosinamine-fatty acid salts in situ in the bronzing liquid upon addition of the bronze, it is preferred to form the fatty acid salt of rosinamine directly upon the copper bronze powder, and following this step to make the bronzing liquid by admixture of the treated bronze powder and lacquer solution.

Having described my invention, what I claim is:

1. A copper-containing bronze powder of improved stability characteristics which comprises a major quantity of a copper containing bronze powder and in intimate contact therewith at least 0.5% but not more than about 5% by weight of said metal powder of an organic compound selected from the group consisting of water insoluble long chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms and a water-insoluble rosinamine.  
2. A copper containing bronze powder characterized by improved stability when in contact with nitrocellulose lacquers in solution in volatile organic solvents which comprises a copper containing bronze powder in intimate contact with a mixture containing at least 0.5% but not more than about 5% by weight of said powder of an organic compound selected from the group consisting of water insoluble long chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms and a water-insoluble rosinamine where the weight ratio of the acid to amine is within the range of from 1:7 to 3:1.  
3. A copper containing bronze powder characterized by improved stability when in contact with nitrocellulose.
lacquers in solution in volatile organic solvents which comprises a copper containing bronze powder in intimate contact with at least five tenths of a percent but not more than about five percent by weight of said powder of an organic compound selected from the group consisting of water insoluble long chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms and a water insoluble rosinamine where the weight ratio of acid to amine is within the range of from 1.5 to 2:1.

4. As in claim 3, where the alicyclic hydrocarbon acid is napthenic acid.

5. As in claim 3, where the long chain aliphatic acid is stearic acid.

6. As in claim 3, where the long chain aliphatic acid is myristic acid.

7. As in claim 3, where the long chain aliphatic acid is palmitic acid.

8. As in claim 3, where the long chain aliphatic acid is lauric acid.

9. As in claim 3, where the rosinamine is a primary rosinamine.

10. A copper containing bronze powder characterized by improved stability when in contact with nitrocellulose lacquers in solution which comprises a copper bronze containing powder, from one half a percent to not appreciably more than five percent of an organic compound selected from the group consisting of water insoluble long chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms and from 0.5% to not more than about 10% by weight of said powder of a primary rosinamine.

11. As in claim 10, where the alicyclic hydrocarbon acid is napthenic acid.

12. As in claim 10, where the long chain aliphatic acid is stearic acid.

13. As in claim 10, where the long chain aliphatic acid is myristic acid.

14. As in claim 10, where the long chain aliphatic acid is palmitic acid.

15. In nitrocellulose lacquer solutions in organic solvents containing copper bronze metallic pigments coated with a lubricating organic acid selected from the group consisting of water insoluble long-chain aliphatic and alicyclic hydrocarbon acids containing from 8 to about 32 carbon atoms in association with said copper bronze powders, the method of increasing the useful life of the above described liquid coating compositions which comprises including therein during manufacture and prior to storage, from 0.5% to not more than about 8% by weight of the copper bronze powder in said coating composition of a water insoluble rosinamine.

16. A method of increasing the useful life of copper bronze powder-containing nitrocellulose lacquers in solution in organic solvents which comprises including with the copper bronze, nitrocellulose lacquer solution and the 0.5% to 5% by weight of said bronze of lubricating fatty acids associated with said copper bronzes from five tenths of a percent to not more than about 10 percent by weight of the copper bronze powder of a primary rosinamine.

17. A method of increasing the useful life of copper bronze powder containing nitrocellulose lacquers in solution in organic solvents which comprises including with the copper bronze, nitrocellulose lacquer solution and the 0.5% to 5% by weight of said bronze of stearic acid associated with said bronze from five tenths of a percent to not more than about eight percent by weight of said bronze of a primary rosinamine.

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