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COPPER PIGMENT

Sidney B. Tuwiner, Flushing, N. Y., and Dwight A. Dodge, Baltimore, Md., assignors to Phelps Dodge Corporation, New York, N. Y., a corporation of New York

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This invention is concerned with the production of copper pigments and more particularly with the preparation of true green copper pigments of good intensity and stability.

Green pigment-like compounds may be prepared from copper salts of organic acids, such as succinic acid. Such compounds, however, are deficient in shade and intensity of color. For example, cupric salts of such organic acids, even when in the required physical condition for use as pigments, have low color strength and are a bluish green rather than a true green color.

It is an object of the present invention to provide an improved method for the production of pigments including organic copper compounds. It is also an object to provide a procedure for producing copper pigments of true green color and of good intensity and stability. Another object is to provide an improved copper pigment comprising a mixture of organic copper compounds and a colloidal dispersion of cuprous oxide. Other objects will become apparent.

We have found that compositions comprising organic copper compounds and containing both cuprous and cupric copper give pigments of good physical properties and chemical stability. For instance, a pigment composition containing submicrocrystalline normal copper succinate, amorphous basic copper succinate and submicrocrystalline cuprous oxide, gives a pigment of true green color and of good intensity and stability.

Such a product may be prepared, for example, by coprecipitating cupric carbonate and a cupric salt of a dibasic acid having at least two carbon atoms between the carboxyl groups and heating the precipitate. For example, a mixed salt of copper carbonate and succinate may be precipitated. The precipitate may be dried and the dried precipitate may be heated sufficiently to liberate carbon dioxide and combined water. During this treatment cuprous oxide is apparently formed by a thermal decomposition of the amorphous basic copper succinate, or from its succinate-carbonate precursor, leaving a pigment containing normal copper succinate, amorphous basic copper succinate with cuprous oxide colloidal dispersed within the basic copper succinate.

As a specific example of the production of such a pigment, 67½ grams of anhydrous sodium carbonate was added to a water solution containing 50 grams of succinic acid. After the effervescence had ceased, the solution was cooled and a saturated aqueous solution containing 158 grams of blue vitriol crystals was added, the solutions

at the time of mixing being at room temperature (about 70° F.). The resulting blue green precipitate, which contained about 98% of the copper added in the form of coprecipitated cupric succinate and cupric carbonate, was air dried for 48 hours on a steam bath, where the temperature of the material reached about 140° F. The dried powder was then heated at a temperature of 470° F. in an atmosphere of nitrogen with sufficient stirring to promote even heating throughout the mass. A vivid green pigment of good color strength was obtained. The pigment gave an ultimate analysis of 48.87% cupric oxide, 7.17% cuprous oxide, the balance, 43.96%, being assumed to be a succinic anhydride.

In the process of heating at 470° F., the carbonate originally present was decomposed to liberate carbon dioxide. Water was also evolved, both from the physical and chemical combination. A partial reduction of the copper also occurred, the organic constituent of the solid probably suffering partial oxidation and thus accounting for the cuprous oxide in the final product. This product, after heating at 470° F., is stable to moisture and to the elements. It is also fairly stable to heat at temperatures below about 450° F. and is more stable to most reagents than before the heating. It has a high tinting strength and shows good durability in oil paints.

The coprecipitated blue-green combination of copper succinate and copper carbonate, the preparation of which is described in the example above, after drying at 140° F., was subjected to X-ray examination for crystal structure. The X-ray photograms obtained were practically identical with that for normal cupric succinate and did not indicate the presence of copper carbonate, but the chemical analysis showed that the precipitate contained much more cupric copper than normal cupric succinate. This would indicate that normal cupric succinate is present in the succinate-carbonate precipitate in crystalline form associated with a form of copper carbonate, or some combination of copper carbonate with copper succinate, which is amorphous, since only an amorphous material would produce no X-ray photogram lines. The dried material, after being heated to 470° F. in an atmosphere of nitrogen, again showed the identical lines of normal cupric succinate in addition to diffuse lines corresponding with those of cuprous oxide. No lines corresponding with cupric oxide were obtained, but the cupric copper was in excess of that in normal cupric succinate. Heating to 450° F. in an inert atmosphere was without effect and