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MANUFACTURE OF FLAKE COPPER POWDER

Othon Adolf Ziehl, Union, N. J., assignor to Metals Disintegrating Company, Inc., Elizabeth, N. J., a corporation of New Jersey

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This invention relates to an improved method of producing metallic "bronze" paste or powder pigment of copper and copper alloys for paints, etc., whereby the resulting products have superior leafing properties imparted to them, their color is improved, the flaking out of the metal particles facilitated, and the product, whether in the dry powder or the paste form, is desirably stable in respect to the excellent and improved qualities before-mentioned. Good leafing properties give high covering power and at the same time produce a mirror-like surface having high reflecting power tinted by the nature of the metal used.

The preferred method of manufacture comprises an impact-ball-milling operation, wherein particles of convenient size are subjected to impact comminuation by suitable media, such as steel balls; the metal particles being charged into the ball mill together with a liquid solvent such as mineral spirits carrying, probably in solution, a leafing agent, such as stearic or palmitic acid, the whole charge forming a sludge. Following in general the directions of U. S. Patent to Hall #2,002,891, the metal particles are flaked out and reduced to a size suitable for application as a paint pigment or for other similar uses, and simultaneously the property of leafing is imparted to the flakes. After this milling operation, the sludge is removed from the mill and ball charge as by a screening or centrifuging operation, or preferably by introducing an additional quantity of the liquid solvent to the mill and washing the diluted sludge from the mill and ball charge. If the sludge, so separated, contains an amount of the solvent excessive for the intended commercial application of the product—as is usually the case—the excess solvent is readily removed as by a filtering or centrifuging operation, etc., and the material brought to paste form. In case a dry flake powder is desired, the solvent may be completely removed by evaporation under carefully controlled temperature conditions, without impairment of the leafing property; it being desirable to carry out such an operation in a vacuum or neutral atmosphere, although this precaution is not necessary providing the temperature is held sufficiently low.

I have found that the methods best adapted for the production of "bronze" pigments vary greatly with the metal treated. For example, wet grinding of aluminum gives the best results with an oxygen-containing atmosphere. For lead, zinc and tin the grinding should take place in a mixture of oxygen and either carbon dioxide or sulphur dioxide. For copper, however, the subject of the present invention, optimum covering power and coefficient of reflection are secured by wet grinding in an inert or at least an oxygen-free atmosphere, such as carbon dioxide, nitrogen and combustion gases.

An inert or oxygen-free atmosphere is also useful in the case of alloys containing large amounts of copper and the term "copper" is intended to include alloys consisting chiefly of copper. Where, however, some other metal, such as zinc, is the preponderating constituent the atmosphere should be such as to give best results with such other metal or a compromise made between the conditions most satisfactory for such other metal and those best for copper.

The presence of oxygen during the milling operation is undesirable. Its effect appears to be due to chemical reactions of some kind, since, when oxygen is present during the milling operation, it is absorbed, probably with the production of copper oxide.

It is also important to keep down the proportion of oxide in the copper feed. A satisfactory product is obtained when the feed contains 0.2% oxygen or less in the form of oxide. Above that percentage the product becomes progressively duller, i. e., its coefficient of reflection decreases.

Not only does oxygen in the mill atmosphere during milling or originally present as oxide in the feed result in a dull product, but it also appears to give a product which is less stable than that obtained by grinding oxide-free feed in a carbon dioxide or other oxygen-free atmosphere. The carbon dioxide, for example, retards any subsequent oxidation and also the settling out of the copper from the paste vehicle when the final product is a paste.

To render the powder suitable for use as a pigment it should not only be flaked, i. e., comminuted in the form of flakes or plates to give it high "covering power," but also it should be treated with a "leafing" agent, which appears to act by causing all or a part of the flakes to float as a nearly continuous layer on the surface of the vehicle in the same manner as a greasy needle will float on the surface of water.

The flaking and leafing operations can take place successively or concurrently. Most conveniently they are carried out concurrently, especially where, as in the present invention, these operations are carried out in an inert atmosphere.

Even where the resulting product is to be in dry form, it is preferable to mill wet, i. e., in the

presence of a suitable volatile vehicle, such as paint thinner, and then dry the product, instead of milling dry. One reason for the superiority of wet milling is that it facilitates the coating of the particles by the leafing agent. Using a leafing agent soluble in the thinner used in the milling operation, it is rapidly brought into contact with the fresh metal surfaces produced by the flaking operation. The coating of the metal surfaces is probably due to adsorption and/or chemical reaction of the leafing agent at such surfaces.

Proper flaking conditions may be judged by the manner in which the sludge in the mill clings to the balls during and at the end of the milling period. When the sludge does not coat the balls properly, that is, when the shiny surface of the balls shows through the sludge, the paste product nearly invariably proves unsatisfactory. From the extent of coating on the balls, the properties of the product can be accurately judged. This coating phenomenon, of course, ties up with the development of a leafing film on the surface of the particles. Proper formation of this film will result in a uniform mixture of metal particles and vehicle. This latter condition exists in the mill when atmospheres of carbon dioxide or of nitrogen are maintained in the mill during the production of the copper paste. Small increments of oxygen added to these gases will gradually diminish the uniformity with which the balls are coated by the dispersed copper-vehicle mixture, and the products are correspondingly inferior.

In practice it is impossible to exclude all oxygen, and the best that can be done is to approach zero oxygen concentration as nearly as possible. The words "free from oxygen" occurring in the claims are to be understood as meaning an approach as near as may be practicable to zero concentration of oxygen.

Once the leafing film is formed and the copper particles are no longer subjected to milling, they are reasonably stable towards the oxygen in air at room temperature, whether the copper flakes are in paste or dry form. Contact with warm air should be avoided, however, especially when the air is humid.

Temperature also is an important factor in producing the highest grades of bronze powders. For copper the temperature of milling should be considerably above normal atmospheric temperature, usually above 50° C. and better still over 60° C. up to 120° C. or higher. This is true even in the case of milling in air, in spite of the fact that the chemical activity of the oxygen of the air increases as the temperature rises. My tests have shown that copper milled in an air atmosphere at 50° or below is inferior to that milled at 60° C. or above. However, the latter product is inferior to that milled at room temperature in an inert atmosphere.

The degree of temperature and also its duration have a deciding effect upon the shade of color of the finished flake metal product. In other words, the color desired in the finished product, starting with one and the same metal feed, may, within limits, be regulated by the degree of temperature employed and the length of time over which the particular temperature is maintained. I have also found that if the temperature is dropped from above 60° C. to below 40° C. during the last part of the milling operation, the color of the product is more nearly that of ordinary burnished copper. If the temperature remains high to the end, the product is a bright pink rather than the color usually ascribed to copper.

In carrying the method into effect, comminuted copper and a vehicle, like mineral spirits, containing in solution a small amount of stearic acid as an example of a "leafing agent," is introduced into the mill. The air in the mill is then exhausted and replaced by a suitable inert gas, such as carbon dioxide, nitrogen, or combustion gases, and milling takes place under regulated temperature conditions as hereinbefore and hereinafter suggested (see Example I and Example II).

After the milling operation is completed, more mineral spirit is added to the sludge in the mill to make it more fluid and hence more readily decanted away from the balls. Any paste adhering to the balls may be washed off with more mineral spirits, so that the average copper content of the ball mill product may be around 30%. This ball mill product is then conveyed to a filter press, where a cake having a copper content of about 88% to 90% is produced. If a paste is required, enough mineral spirits is added to drop the copper percentage to around 85%. If a dry powder is desired, the cake is dried in a vacuum at a temperature of about 160°–200° F. and allowed to cool down to room temperature under vacuum.

When additional vehicle is added to the filter cake to make a paste, this vehicle, instead of being a mineral spirit, may, to advantage, be an aromatic compound, like toluol, when the paste is to be used with cellulose ester or Bakelite type compositions to aid the compatibility of the paste for such compositions.

I have found it advantageous to saturate the mineral spirits used initially and in the additions and washouts with carbon dioxide before use. This procedure gives enhanced mirroring, and greater stability, with respect to both consistency and also to oxidation.

Mineral spirits is the preferred milling liquid because it is a common constituent of varnish, it is economical to use, its boiling range is such that there is no excessive loss by evaporation or great fire hazard, though it may develop some vapor pressure, depending on the temperature, which will assist in preventing invasion of the mill by oxygen; and yet the liquid can readily be removed by evaporation when a dry product is desired. However, in place of mineral spirits other thinners may be employed in the mill, for example, xylene, toluene, benzene, heavy mineral oil, naphtha, turpentine, nitrobenzene, trichlorobenzene, and similar hydrocarbon solvents and their derivatives, especially where the paste is to be used with cellulose ester or Bakelite compositions.

Another reason for employing mineral spirit as the milling liquid is that it is a relatively poor solvent for the leafing film that is formed on the flakes during the milling operation, so that likelihood of sloughing off of the film is at a practical minimum.

In general, the higher the milling temperature the better the mirroring of the resulting flake product. The temperature is limited, from a practical point of view, by the boiling point of the particular liquid employed. For example, the boiling point range for mineral spirits is from 150 to 200° C. Using mineral spirits as the grinding vehicle, the milling temperature should, therefore, not be greatly in excess of 120° C. Should

benzene (B. P. 80° C.) or toluene (B. P. 110° C.) be employed, the temperature would necessarily have to be very considerably lower. On the other hand, by using higher boiling point liquids, like nitrobenzene (B. P. 210° C.), the milling temperature may be raised above 120° C.

The milling operation generates heat. Thus, starting a run with a three-foot diameter mill at room temperature, the temperature will go up to about 80° C. in three hours and to 110° C. in six hours. On starting a new run, with the mill still hot from the preceding run, the temperature after three hours may be 110° C. or more. The larger the mill the less heat is dissipated into the surrounding air and hence the higher the equilibrium temperature.

It has been the practice heretofore in the manufacture of aluminum bronze, for example, to keep the temperature at 50° C. or below by water-cooling the mill. As distinguished from that practice, in cases where the heat due to the milling operation is insufficient to meet the requirements of my process I apply additional heat in any preferred way, and this may be done during the early part of the run or throughout the run, as may be necessary to maintain or vary the temperature conditions in accordance with the desiderata of this invention; and, especially where a readily volatile liquid like toluene is used, the mill may be artificially cooled during the latter part of the run to prevent the temperature exceeding, say, 80° C.

Example I

22 lbs. of 100 mesh copper is fed into a mill, 36" dia. and 6" wide, containing 280 lbs. balls of ¼" to ⅜" dia. To this is added 185 g. stearic acid and 4400 cc. mineral spirits. The mill is rotated at a speed that permits cataracting or about 45 R. P. M. for 7 hours at a temperature of 80° C., the while there is maintained within the mill an atmosphere of carbon dioxide. After completion of milling, the sludge in the mill is washed out with several portions of mineral spirits and the solids in the mill discharge then concentrated by a filtering operation to a metal content of about 90%. This filter cake may then be adjusted with fresh thinner to a paste of proper consistency (85% metal content) or else it may be dried under carefully controlled conditions of temperature and atmosphere. Of course, modifications may be made, such as adding only 2800 cc. mineral spirits initially and then making periodic additions during the run, say 400 cc. portions at the end of the second, third, fourth, and fifth hour of milling.

Example II

400 lbs. of copper (100 mesh) are charged into a 3 ft. dia. by 9 ft. mill containing 5000 lbs. balls. To this is added 10 lbs. stearic acid (2½% on the copper) 10 gals. mineral spirits at the start, and a total of 10 gals. added during the run in 2½ gallon portions, at 1½, 2½, 3½, and 5 hours. The temperature is brought up to 75° C. during the first two hours and maintained at that level until the end of the sixth hour. Water is then sprayed on the mill for 45 minutes, bringing the temperature down to 30° C. Milling is continued for another 15 minutes (total 7 hours) without the water spray to get rid of the water on the mill shell, the temperature during this period remaining constant at 30° C. Milling is then discontinued and the sludge in the mill washed out with six portions of 50 gals. each of mineral spirits, the mill discharge filtered and the filter cake either adjusted to 85% paste or dried in a rotary vacuum drier. Throughout the milling operation there is maintained within the mill an atmosphere of carbon dioxide.

I claim:

1. A wet-milling method of producing leafing copper bronze pigment, which consists in milling copper particles so as to reduce them to flake form, in a mill with a liquid hydrocarbon solvent carrying a leafing agent in solution, while maintaining in the mill an atmosphere free from oxygen and a temperature not lower than about 60° C., but below the point at which boiling occurs in the solvent, substantially as set forth.

2. The method set forth in claim 1, in which the operating temperature is of the order of about 75° C.

3. The method set forth in claim 1, in which the solvent is saturated with an inert gas.

4. A wet-milling method of producing leafing copper bronze pigment, which consists in milling copper particles so as to reduce them to flake form, in a mill with a liquid hydrocarbon solvent carrying a leafing agent in solution, while maintaining in the mill an atmosphere free from oxygen, and a temperature for the first and major part of the flaking operation, not lower than about 60° C., but below the point at which boiling occurs in the solvent, and reducing the temperature for the final part of the flaking operation to a point below 50° C., substantially as set forth.

5. The method set forth in claim 4, in which the temperature for the major part of the operation is of the order of about 75° C., and for the final part of the operation about 30° C.

OTHON ADOLF ZIEHL.