

UNITED STATES PATENT OFFICE

2,462,870

ELECTRODEPOSITION OF COPPER

Frank R. Keller, Coraopolis, Pa., assignor to General Motors Corporation, Detroit, Mich., a corporation of Delaware

No Drawing. Application July 9, 1942,
Serial No. 450,279

4 Claims. (Cl. 204—52)

1

The invention relates to the electrodeposition of copper and includes a method of producing electrodeposited coatings as well as the composition of the electrolyte employed. The principal object of the invention is the production of a copper deposit having a high degree of brightness together with other desirable properties. A further object is the provision of an improved electrolyte and such control of the operating conditions as will enable the operator to obtain the desired results.

With these and other objects in view, as will appear herein, the invention comprises an acid bath in which the principal copper salt is copper sulphate and to which are added certain addition agents capable of changing entirely the character of the deposited copper as compared with that ordinarily obtained from copper sulphate electrolytes.

The well-known advantages of the copper sulphate bath have led to its extensive use. The usual deposit, however, is quite dull and rough, resulting in the necessity of buffing or polishing operations if a bright surface is desired. Such operations are objectionable for various reasons, among which are the resultant wastage of metal and the reduction in the thickness of the coating especially on more exposed portions liable to more severe contact with buffing agents. Furthermore, buffing is an expensive process both as to labor and materials and may be practically impossible on complicated surfaces.

The more recently introduced processes of electroplating other metals in bright form, e. g., nickel and chromium, whereby buffing has been largely eliminated, have served to increase the interest in the possibility of a similar result with copper, especially as copper is quite generally used as an undercoating for the other metals. Great difficulty has been encountered, however, in obtaining bright or even semi-bright deposits from the acid copper sulphate bath.

In accordance with the present invention, bright or semi-bright copper deposits are secured by the combined and coordinated effect of two addition agents, each of which has been previously suggested and used but, so far as I am aware, have not before been employed in conjunction, for example, molasses and thiourea.

Molasses has been used in copper sulphate plating baths for the alleged purpose of smoothing the deposit to some extent and facilitating buffing, but is incapable of producing a truly bright deposit. Thiourea has more recently been found to be an effective brightening agent in a copper

2

sulphate bath but requires, if used alone, very narrowly limited conditions if a uniformly bright plate is to be obtained, and some control agent has been found desirable to improve the range of effective action of the thiourea.

I have discovered that molasses in small quantities exerts a remarkable effect upon the action of the thiourea. In the first place, it increases the tolerance of the bath for thiourea so that larger amounts of thiourea can be used with corresponding increase of the brightening effect.

Furthermore, the addition of molasses increases the range of current densities within which brightness is obtained. Also it enables bright deposits to be secured at higher temperatures than is possible with thiourea alone, thus rendering the bath available for bright plating without special cooling means. Mottled, cloudy, and striated effects may be substantially completely eliminated. Standard production output can be plated directly with bright nickel and yield commercially satisfactory brilliance of the nickel coating without first buffing or polishing the copper surface. Even though conditions are not so carefully regulated as to produce absolute brilliance, the deposits readily obtained in commercial practice have such a high degree of brightness that only a slight polishing operation, more a "wipe" than a buff, is needed to produce a brilliant surface. Such "wiping" operation is proven by tests to remove only a negligible and scarcely measurable amount of metal.

The content of the bath as to copper sulphate and sulphuric acid is not critical. Such content may vary as in standard practice, for example, an aqueous bath containing from 50 to 250 grams per liter of the technical copper sulphate ordinarily supplied for plating and 5 to 100 grams per liter of sulphuric acid. In practicing the present invention, however, a relatively low content of acid is regarded as preferable, for example, not more than approximately 50 grams per liter.

The content of molasses, which may be the ordinary commercial grade known as "baking molasses," may vary considerably within the approximate range of 0.01 to 2 grams per liter. For best results, less than 1 gram per liter is preferable and about 0.2 to 1 gram is recommended.

The thiourea content may also vary considerably within an extreme range of 0.002 to 5 grams per liter. For best commercial results, however, a fairly narrow range of approximately 0.01 to 0.1 gram per liter is recommended.

Relatively low bath temperatures are desirable. Temperatures of 70° to 80° F. have been found

3

satisfactory in practice. If optimum brightness is to be obtained, however, a temperature at least as low as 60° to 65° may be preferable. Lower temperatures may be secured by suitable cooling. Vigorous agitation such as may be produced by introduction of air has been found useful in promoting high rate of deposition and uniformity of brightness.

The current density may vary widely on different parts of the work without seriously affecting the character of the deposit. It may, for example, be as high as 100 or more amperes per square foot in places, but an average of approximately 50 to 75 amperes has been found satisfactory with suitable agitation.

The following is given as an example of a typical installation:

Copper sulphate-----	grams per liter--	210
Sulphuric acid-----	do-----	30
Molasses-----	do-----	0.80
Thiourea-----	do-----	0.04
Temperature 70° F., current density 70-75 amperes per square foot.		

The physical structure of the deposited metal is quite different from that presented by metal deposited from the ordinary copper sulphate bath. The crystal growth in the latter case is clearly perpendicular to the base metal whereas the metal deposited in accordance with the present invention lies in layers parallel with the surface and without projecting points or nodules. In fact, should the surface of the base metal not be entirely smooth before plating begins, the surface of the deposit seems to become more even and bright as the deposition proceeds.

Because of the character of the deposit as well as the ease of adapting the procedure to the standard copper sulphate baths, the process presents marked advantages in the deposition of copper, either for protection of surfaces or recovery of metal.

I claim:

1. A bath for electrodeposition of copper in bright or semi-bright condition consisting essen-

4

tially of an aqueous solution containing, per liter, approximately 210 grams copper sulphate, 30 grams sulphuric acid, 0.8 gram molasses and 0.04 gram thiourea.

2. A bath for electrodeposition of copper in bright or semi-bright condition consisting essentially of an aqueous solution of copper sulphate and sulphuric acid to which has been added approximately, per liter, 0.01 to 2 grams molasses and 0.002 to 5 grams thiourea.

3. A bath for electrodeposition of copper in bright or semi-bright form, said bath containing in aqueous solution 50 to 250 grams copper sulphate and 5 to 50 grams sulphuric acid per liter and including, as essential ingredients for production of brightness, 0.1 to 1 gram molasses and 0.01 to 0.1 gram thiourea per liter.

4. A bath for electrodeposition of copper in bright or semi-bright condition comprising an aqueous solution of copper sulphate, 50 to 250 grams per liter and sulphuric acid 5 to 100 grams per liter and containing as essential ingredients for production of brightness molasses 0.1 to 2 grams per liter and thiourea 0.002 to 5 grams per liter.

FRANK R. KELLER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,464,149	Classen-----	Aug. 7, 1923
1,465,034	Antisell-----	Aug. 14, 1923
1,544,726	Colcord-----	July 7, 1925
1,805,920	Muschler-----	May 19, 1931
1,903,860	Gockel-----	Apr. 18, 1933

OTHER REFERENCES

Holdeman: 1936 Thesis at Purdue University, West Lafayette, Indiana, pp. 14, 23, 24 and 36.
Metal Industry, Nov. 29, 1940, p. 433.
Metal Finishing, Sept. 1942, p. 457.