

1

3,460,977

MECHANICAL PLATING

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9 Claims

ABSTRACT OF THE DISCLOSURE

In mechanical plating processes outstanding plating efficiency, uniformity, cohesion, coverage, brightness, and smoothness of the applied coating are obtained when effective amounts of certain surfactants, or blends thereof, are present. These surfactants include anionic or non-ionic dispersants such as polymerized alkyl aryl sulfonate, alkyl adducts of diphenyl oxide, molecules having a hydrophobic polyoxypropylene nucleus having hydrophilic polyoxyethylene chains attached thereto, polyoxyethylene glycol adducts of alkyl phenols, and amphoteric salts of long-chain alkyl beta-amino acids; cationic quaternary ammonium derivatives having heterocyclic hydrophilic nitrogen-containing rings and hydrophobic alkyl groups are also highly effective.

This invention relates to promoter chemicals for facilitating the mechanical plating of finely divided metal particles onto metallic substrates as smooth, dense, adherent, lustrous protective and/or decorative platings or coatings.

The process of mechanical plating has been known for perhaps a quarter of a century, but it has become of increasing significance during the last decade. The broad principles of the process are well known; see, e.g., British Patent No. 534,888, U.S. Patents No. 2,689,808, and Re. 23,861, and other patents and publications. The process is typically carried out by placing in a tumbling barrel metallic parts to be plated, plating metals in the form of minute malleable particles, impact media such as glass beads and cullet, and water. A variety of inorganic and organic chemicals may also be added to promote the mechanical plating action. As the tumbling barrel is rotated, the plating metal particles are hammered against the surface of the metallic parts to be plated, the impact media and the parts themselves serving to flatten the metal particles into a continuous coat. A properly applied mechanical plating is smooth, uniform, and provides excellent corrosion protection, at the same time employing simple and inexpensive equipment, particularly when contrasted to electroplating apparatus. In order to simplify the mechanical plating operation and to permit the use of unskilled personnel, it is desirable to conduct mechanical plating as a batch process, in which all the plating materials and promoters are added at the start of the operation. My invention is directed to the provision of promoter compositions which are particularly effective in batch operations, whether added only at the start of the plating operation or at various times throughout the cycle.

As ingredients for the mechanical plating promoter compositions of my invention, I include a dispersant chemical (defined in greater detail hereinafter), an acidic material (or one which hydrolyzes to yield hydrogen ions), and, optionally, such additives as fillers, metal salts, adsorbents, absorbents, or chelating agents. Mold release agents (and, if desired, binder materials) may also be included to facilitate manufacture of plating promoter

2

chemical in the form of cakes, or bars, in the manner taught in the copending application of my associate John Simon, Ser. No. 41,022, filed July 6, 1960, now abandoned, a continuation-in-part of which application is now U.S. Patent 3,328,197, having the same assignee as the present application.

I am aware of the fact that others have suggested the use of detergents and wetting agents in mechanical plating operations, but I have found most detergents totally unsuited for my purposes. Detergents function primarily by wetting a surface, whereas dispersants are designed to prevent or break up flocculated aggregates. I am likewise aware that others have suggested the use of film-forming agents in mechanical plating operations. Some excellent dispersants form no more than a monomolecular layer on a surface and hence are not film-forming in the normal sense of that term. My invention, then, involves the discovery that certain strong dispersants, most of which are neither detergents nor film-forming agents, are unusually and unexpectedly effective aids in mechanical plating operations.

Dispersants which I have found to be unusually effective plating promoters, yielding outstanding mechanical platings, include salts of polymerized alkyl aryl sulfonic acids such as lignin sulfonates or higher alkyl adducts of diphenyl oxide; polymers having a hydrophobic polyoxypropylene-terminated nucleus with a plurality of hydrophilic polyoxyethylene glycol-terminated chains attached thereto, such as the "Pluronics" or "Tetronics"; polyoxyethylene glycol adducts of alkyl phenols; quaternary ammonium derivatives having heterocyclic hydrophobic nitrogen-containing rings and hydrophobic alkyl groups, such as 1-(2-hydroxy alkyl)-2-n-alkyl-1 benzyl-2-imidazolium chloride or compounds having hydrophilic morpholinium alkosulfate and hydrophobic higher aliphatic groups; and amphoteric salts of long chain alkyl beta amino acids.

A wide variety of acidic, or acid-engendering, materials, may be used in the practice of my invention, provided the dissociation constant is at least equal to about 10^{-7} . If the dissociation constant exceeds about 10^{-2} , a buffering or protective material should be added to prevent the acid and the plating metal particles from consuming each other before adequate plating can take place. The function of the acidic material in this composition is to clean the surface of both the metallic substrate to be plated and the plating powder, generally by the removing of oxide scale or other material which would prevent intimate contact between the plating metal particles and substrate, this essential cleaning action also tends to cause premature agglomeration of the plating particles, the strong dispersants described herein holding this undesirable phenomenon in check, a concept which is well known. Among the many acids which may be used with effectiveness are the following: acetic, adipic, benzoic, 1-ascorbic, butyric, citric, crotonic, diglycolic, formic, gallic, gluconic, hydrochloric, lactic, maleic, malic, phthalic, propionic, succinic, sulfanilic sulfuric, tartaric, etc. The soluble acidic salts of such acids also prove effective in this operation. Acidic or acid-engendering materials include aluminum chloride, aluminum sulfate, ammonium bifluoride, sodium bisulfate, zinc chloride, zirconium sulfate, and many others.

Regardless of the dispersant used, it is necessary that it be at least "very slightly soluble" as that term is defined in Hackh's Chemical Dictionary, i.e., that one part of dispersant dissolves in from 1,000–10,000 parts of water or

less, in ten minutes. The exact amount of dispersant used depends upon the relative molecular weight of the acidic material and dispersant, the strength of the acidic material, the effectiveness of the dispersant, and the particular system involved. The minimum amount of dispersant which is effective in combination with the acidic cleaning agent has been found to be as low as $\frac{1}{20}$ by weight of the acidic material in certain cases, but generally is somewhat higher.

As a guide to securing the proper ratio between dispersant and acidic material I have found is convenient to relate the amount of dispersant to the amount of available hydrogen ion supplied by the acidic material. As a rule of thumb, at least 0.05 gram of dispersant, and generally at least 1.5 grams, is required for every gram mol of available hydrogen. "Available" in this context is intended to mean that the acidic hydrogen has a dissociation constant of at least 10^{-7} . It will thus be apparent that some polybasic acids have both "available" and "unavailable" hydrogen.

In evaluating the effectiveness of a given dispersant in producing good mechanical platings, I have found it convenient to consider six criteria—plating efficiency, uniformity, cohesion, coverage, brightness, and smoothness of the mechanical plating. The relative significance of these criteria varies with the specific end result sought, but I generally assign an arbitrary value of 5 for outstanding performance and 0 for extremely poor performance. According to this somewhat subjective and empirical technique, a "perfect" mechanical plating would be assigned the value of 30. Generally speaking, a rating of 22 is considered fair, and 25 or more is considered very good.

As a guide to interpreting the criteria specified in the preceding paragraph, I offer the following brief statement of qualities which would receive a 5 rating. Plating efficiency—at least 90% of the plating metal particles are utilized. Uniformity—thickness variation of no more than $\pm 10\%$ over the plated object. Cohesion—plating is not removed when scored with a razor blade and tested by applying a strip of pressure-sensitive adhesive tape and quickly removing it. Coverage—none of the uncoated surface shows through when examined under $100\times$ magnification. Brightness—surface closely resembles polished zinc. Smoothness—surface is regular, with no signs of nodularity.

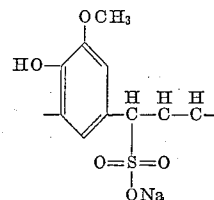
The following examples illustrate the use of various compositions of promoter chemical materials in the practice of my invention. These examples are intended to be illustrative only, and numerous equivalents will suggest themselves to the man ordinarily skilled in the art.

Example 1

To a 1.2-gallon plastisol-lined hexagonal plating barrel was added 1,000 grams of $\frac{3}{8}$ -inch mild steel washers which had previously been cleaned in an acid solution and flash-plated with copper. To the barrel was then added 2,824 grams of spherical glass impact media (4 parts 4 to 6 mesh, 2 parts 12 to 14 mesh, and 1 part 90 to 100 mesh). Sufficient water at room temperature was then added to bring the liquid level about $\frac{1}{2}$ inch above the solid mixture. Next, a promoter chemical pellet containing 10.6 grams of promoter chemical, prepared by pressing at 8,000 p.s.i., was added. The pellet contained 5 grams of citric acid, 5 grams of diammonium citrate, 0.2 gram of stearic acid, and 0.4 gram of purified sodium lignosulfonate (available commercially from the Marathon Chemical Company as "Marasperse N"). 20 grams of 3-micron zinc dust was also added to the barrel, which was thereafter rotated at 54 r.p.m. for one hour. The washers were provided with an excellent appearing zinc coat which displayed extremely good cohesion, and received a quality index rating of 25. In the absence of the "Marasperse N," the zinc coating was rough, poorly dis-

tributed, and generally unattractive, receiving a quality index rating of 13 to 15.

The purified sodium lignosulfonate of Example 1 is representative of several dispersants which are derived from wood. The structure of lignosulfonate has not been determined exactly, but it is believed to be a high polymer having a molecular weight of about 10,000 and including the following repeating unit:



This product may also be termed a salt of a polymerized substituted alkyl aryl sulfonic acid, where the aryl group is substituted benzene. I have found that about 1.5 grams of such dispersants per gram mol of available hydrogen generally represents the approximate minimum amount for effective plating.

The examples tabulated below were carried out in exactly the same manner as Example 1, with the substitution of different dispersants, all wood derivatives, for the purified sodium lignosulfonate:

Example	Dispersant	Grams dispersant	Quality index
2-----	Purified calcium lignosulfonate ("Marasperse C").	0.4	23
3-----	Purified partially desulfonated calcium lignosulfonate ("Marasperse CE").	0.4	23
4+*-----	Mixed salts of low molecular weight lignosulfonic acids, containing some residual sugars ("Maracarb N").	0.5	28
5+@-----	Ammonium lignosulfonate containing some wood sugars ("Orzan AH-3," available from Crown-Zellerbach).	0.1	26
6-----	Sodium lignosulfonate containing some wood sugars ("Orzan S").	0.4	24
7-----	Ammonium lignosulfonate containing some wood sugars ("Orzan A").	0.4	24

*Citric acid and diammonium citrate of Example 1 replaced by 10 grams salicylic acid.

+ 4-6 mesh impact media of Example 1 replaced by 3-4 mesh glass cullet.

@ Citric acid and diammonium citrate of Example 1 replaced by 5 grams diglycolic acid and 0.5 g. CaCO_3 (Diglycolic acid reacted with CaCO_3 to yield a buffered system).

The preceding examples are directed to wood-derived alkyl aryl sulfonates; other alkyl aryl sulfonates have also proved effective as dispersants. Some such materials are shown in the following examples, each of which was carried out in the same manner as Example 1, with the substitution of the dispersant as noted.

Example	Dispersant	Grams dispersant	Quality index
8-----	Sodium salt of polymerized alkyl naphthalene sulfonic acid (available as "Darvan No. 1," from R. T. Vanderbilt Co.).	0.4	27
9-----	Sodium salt of polymerized substituted benzoid alkyl sulfonic acid ("Darvan No. 2").	0.4	26
10-----	Sodium salt of poly condensed mono-naphthalene sulfonic acid ("Lomar PW," available from the Nopco Chemical Company or "Tamol N" or "Tamol SN," available from Rohm & Haas).	0.7	27
11-----	Sodium salt of sulfonated dodecyl diphenyl oxide ("Benax 2A-1," available from the Dow Chemical Company).	0.4	23

Other dispersants which I have found particularly effective in the practice of my invention are polymers having a hydrophobic polyoxypropylene-terminated nucleus and a plurality of hydrophilic polyoxyethylene glycol-terminated chains attached to the nucleus. Representative of such materials are the Wyandotte Chemical Com-

pany's "Pluronics," which have a hydrophobic polyoxypropylene nucleus, to each end of which is connected a hydrophilic polyoxyethylene glycol chain. "Pluronics" whose nucleus have a molecular weight of at least about 4,000 have been found to produce superior results, while the polymers which fall outside these parameters have been noticeably less satisfactory, and, in some instances, actually worse than no additive at all. Related to the "Pluronics" are the "Tetronics," also available from the Wyandotte Chemical Company. In these materials the nucleus is made up of ethylene diamine having four poly-

ance between the hydrophobic alkyl phenol and the hydrophilic ethylene oxide chain, such that the dispersant properties are enhanced. The following table illustrates dispersants in this family which have proved effective; as in the preceding tables, the process followed was the same as that described in Example 1 unless otherwise noted. Typical dispersants of this kind are the "Surfonics," available from the Jefferson Chemical Company, the "Igepals," available from the General Aniline & Film Corporation, and the "Hyonics," available from Nopco Chemical Company.

Example	Dispersant	Grams of dispersant	Alkyl phenol	Number of EtO units	Quality index
29	"Surfonic N-120"	0.4	Nonyl phenol	12	22
30	"Surfonic N-150"	0.5	do	15	25
31	"Surfonic N-200"	0.3	do	20	24
32	"Surfonic N-300"	0.4	do	30	23
33	"Igepal CO-880"	0.5	do	30	26
34	"Hyonic PE-120"	0.5	Octyl phenol	12	24

+ 4-6 mesh impact media of Example 1 replaced with 3-4 mesh impact media.
*20 grams of zinc powder used in Example 1 reduced to 15.

oxypropylene chains attached thereto, polyoxyethylene glycol terminating each chain. Speaking in general terms, the "Tetronics" are effective at a lower total molecular weight and lower nucleus weight than the "Pluronics." In possible explanation thereof, I offer the suggestion that the effectiveness of a nonionic dispersant depends in part on its ability to prevent contact between the metal plating particles and that this effectiveness is enhanced by the degree of motive hindrance which the dispersant can impart to the particles. This hypothesis is supported by the entangling properties which branched polymers like the "Tetronics" should possess. Empirically I have established that the total molecular weight of an effective surfactant of either the "Pluronic" or the "Tetronic" type should be at least about 4,000/*n*, and preferably at least 5,000/*n*, where *n* is the number of polyoxyethylene glycol chains in excess of 1. Where the molecular weight of the dispersant is sufficiently high (e.g., 25,000 in the case of "Tetronics" and somewhat higher in the case of linear molecules), the minimum amount of dispersant required tends to decrease.

The following table sets forth a series of examples, each made in the same manner as Example 1, except as otherwise noted, demonstrating the utility of various "Pluronics" and "Tetronics":

Ex.	Dispersant	Grams dispersant	Average nucleus M.W.	Average total M.W.	Quality index
12	"Pluronic P-75"	0.4	2,050	4,100	22
13	"Pluronic P-85"	0.4	2,250	4,500	21
14	"Pluronic P-94"	0.4	2,750	4,590	25
15	"Pluronic P-104"	0.4	3,250	5,420	24
16	"Pluronic P-105"	0.4	3,250	6,500	25
17	"Pluronic F-77"	0.4	2,050	6,850	24
18	"Pluronic F-68"	0.4	1,750	8,750	24
19	"Pluronic F-88"	0.4	2,250	11,250	25
21	"Pluronic F-108"	0.4	3,250	16,250	27
22	"Tetronic 304"	0.4	1,000	1,700	23
23	"Tetronic 702"	0.5	3,000	3,850	22
24	"Tetronic 904"	0.5	4,500	7,500	26
25	"Tetronic 707"	0.05	3,000	12,000	24
26	"Tetronic 707"	0.4	3,000	12,000	26
27	"Tetronic 908"	0.05	4,500	27,000	23
28	"Tetronic 908"	0.4	4,500	27,000	26

+ 4-6 mesh impact media of Example 1 replaced with 3-4 mesh glass cullet.

Other dispersants which function effectively in the practice of this invention include certain polyoxyethylene glycol adducts of alkyl phenols, especially nonyl phenols. Polyoxyethylene glycol adducts of nonyl phenol in which the polyoxyethylene glycol chain contains from 12 to 30 ethylene oxide groups have proved outstanding, and if the ethylene oxide chain is much shorter, the results are noticeably inferior. I believe this may be due to the fact that the particular preferred range maintains a nice bal-

Certain cationic surfactants have also been found useful in the practice of my invention. Although these materials function in a more complex manner than the dispersants previously described herein, they effectively bring about the same superior plating result by controlling aggregate formation. Among the most effective are certain hydrophilic heterocyclic adducts of hydrophobic alkyl compounds which contains nitrogen groups, for example, 1-(2-hydroxy alkyl) - 2-n-alkyl-1-benzyl-2-imidazolinium salts, higher alkyl derivatives of morpholinium alkosulfates, and the like. Generally about 1.5 grams of dispersant for every gram mol of available acidic hydrogen is effective. The following examples illustrate such materials.

Example 35

The process of Example 34 was repeated except that 0.5 gram of "Nalquat G-8-13," 1-(2-hydroxyethyl)-2-n-heptadecenyl-1-benzyl-2-imidazolinium chloride, available commercially from the Nalco Chemical Company, was employed as a dispersant and 0.2 gram of SnCl₂ was added. Quality index of the resulting plate was 24.

Example 36

The process of Example 34 was repeated, except that the citric acid and ammonium citrate was replaced with 5 grams of NaHSO₄ and 1 gram of isophthalic acid, the dispersant employed was 0.1 gram of "Nalquat G-8-11"¹, and 0.1 gram of anhydrous SnCl₂ was added. The "Nalquat G-8-11" is similar to the dispersant employed in the preceding example. Quality index of the resulting plate was 25.

Example 37

The process of Example 34 was repeated, except that 0.7 gram of N-soya-N-ethyl morpholinium ethosulfate was employed as the dispersant. (This dispersant is available commercially as "Atlas 271" from the Atlas Chemical Company.) Quality index of the resultant product was 27. N-cetyl-N-ethyl morpholinium ethosulfate ("Atlas 263") may be employed with substantially the same results.

Among the most effective dispersants which I have employed are such amphoteric compounds as the soluble salts of long chain beta amino substituted acids. The following example illustrates such dispersants.

¹ 1-(2-hydroxyethyl)-2-n-alkyl-1 (or 3) benzyl-2-imidazolinium chloride, where the alkyl group is derived from coco fatty acid, which is a blend of alkyl chains ranging from 8 to 18 carbon atoms, the average molecular weight of the dispersant being about 413.

Example 38

The process of Example 1 was repeated except that 0.4 gram of amphoteric disodium N-tallow beta imino dipropionate, available commercially as "Deriphat 154" from General Mills, was used as a dispersant. The quality index was found to be 25.

I have found that certain combinations of surfactants produce synergistic effects. The following examples illustrate such a combination.

Example 39

The process of Example 34 was repeated, except that as a surfactant a blend of 0.1 gram of "Tetronic 707" and 0.2 gram of "Nalquat G-8-11" was employed, and, additionally, 0.2 gram of ethylene diamine tetra acetic acid (EDTA) was added. "Nalquat G-8-11" is similar to the dispersant of Example 35 except for a different alkyl substituent. The EDTA is a known chelating agent, which functions to scavenge stray ions. The quality index of the resulting plate was 30, which is as close to perfection as any mechanical plating products I have ever seen. When only the "Nalquat G-8-11" is employed, the resulting plate has a quality index rating of 28.

Example 40

The process of Example 34 was repeated, except that the dispersing agent employed consisted of 0.1 gram of "Tetronic 707" and 0.1 gram of "Methocel 8000" (methyl cellulose having a viscosity rating of approximately 8000). Exceptional plating efficiency was achieved, and the quality index of the resultant plate was 28.

Although the foregoing examples all involve the addition of promoter chemicals (acid and dispersant) in pellet or bar form, this is merely a matter of convenience. Because of the highly effective dispersing power of the dispersant materials I have disclosed, essentially the same results are obtained when the various promoter chemicals are added in the form of powder or solution. The bar does, however, decrease the rate of acid release, and thus, in effect, cooperates to enhance the effectiveness of less powerful dispersants.

What I claim is:

1. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble anionic dispersant which consists essentially of at least one salt of a polymerized alkyl aryl sulfonic acid, the aryl group being selected from the class consisting of benzene, naphthalene and diphenyl, the amount of said dispersant added being at least about 1.5 grams per gram mol of hydrogen available from said acid.

2. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble nonionic dispersant which consists essentially of a polymer having a hydrophobic polyoxypropylene-terminated nucleus and a plurality of hydrophilic polyoxyethylene glycol chains attached to said nucleus, the amount of said dispersant added being at least about 0.5 gram per gram mol of hydrogen available from said acid.

3. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely

divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble nonionic dispersant consisting essentially of a polyoxyethylene glycol adduct of hydrophobic alkyl phenol selected from the class consisting of octyl phenol and nonyl phenol, the amount of said dispersant added being at least about 1.5 grams per gram mol of hydrogen available from said acid.

4. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble cationic surfactant consisting essentially of 1 - (2 - hydroxy ethyl) - 2 - n - alkyl - benzyl - 2 - imidazolium chloride wherein the alkyl group contains 8-18 carbon atoms, the amount of said surfactant added being at least about 1.5 grams per gram mol of hydrogen available from said acid.

5. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble salt of N-tallow beta imino propionic acid, the amount of said salt added being at least about 1.5 grams per gram mol of hydrogen available from said acid.

6. In a method of enhancing and facilitating the mechanical plating of parts which includes the steps of placing said parts in a plating barrel together with finely divided plating metal, impact media, acid and water and thereafter agitating the contents of the barrel until said parts have been plated with said plating metal, the improvement comprising adding to the contents of said barrel an at least very slightly soluble compound consisting essentially of a hydrophilic morpholinium ethosulfate group and a hydrophobic aliphatic group derived from a naturally occurring fatty acid, the amount of said compound added being at least about 1.5 grams per gram mol of hydrogen available from said acid.

7. The method of claim 2 wherein there is also added a nonionic dispersant having a hydrophobic polyoxypropylene-terminated nucleus with a plurality of hydrophilic polyoxyethylene chains attached to the free end of each polyoxypropylene chain.

8. The method of claim 2 wherein ethylene diamine tetra acetic acid is also added.

9. The method of claim 2 wherein methyl cellulose is also added.

References Cited

UNITED STATES PATENTS

2,847,384	8/1958	Conklin et al.	252—142 XR
2,942,956	6/1960	Kelly	252—142 XR
2,994,664	8/1961	Watcher	252—87
2,999,767	9/1961	Clay et al.	106—1 XR
3,042,621	7/1962	Kirschenbauer ...	252—142 XR
3,116,105	12/1963	Kerst	252—180 XR
3,211,659	10/1965	Pikaar	252—142 XR
3,222,201	12/1965	Boyle et al.	106—285
3,328,197	6/1967	Simon	106—1 XR

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