

72] Inventors **Frank A. Brindisi, Jr.**
Madison;
Theophil J. Wiczorek, West Haven, both
of Conn.

21] Appl. No. **12,134**
22] Filed **Feb. 17, 1970**
45] Patented **Nov. 9, 1971**
73] Assignee **Enthone Incorporated**
New Haven, Conn.

54] **NO RERACK METAL PLATING OF**
ELECTRICALLY NONCONDUCTIVE ARTICLES
23 Claims, No Drawings

52] U.S. Cl. **117/47 A,**
117/5.5, 117/62.1, 117/160 R, 204/30

51] Int. Cl. **B44d 1/092**

50] Field of Search **117/47 A,**
160 R, 62.1, 5.5; 204/30

[56] **References Cited**

UNITED STATES PATENTS

3,443,988 5/1969 McCormack et al. 117/47 A

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—Janyce A. Bell
Attorneys—Elwood J. Schaffer and Roger J. Drew

ABSTRACT: No rerack process for the metal plating of electrically nonconductive articles or objects on vinyl plastisol-coated plating racks, involving contacting the rack prior to racking thereon the nonconductive articles destined to be plated with a liquid lower alkyl formamide, preferably N,N-dimethylformamide, or N-methyl-2-pyrrolidone, or a mixture thereof, for a time sufficient to render the rack substantially nonsusceptible to electroless deposition of metal thereon during a subsequent electroless metal plating step. Consequently the prior requirement of reracking of the articles on clean racks subsequent the electroless metal plating step and prior to the electroplating is eliminated.

NO RERACK METAL PLATING OF ELECTRICALLY NONCONDUCTIVE ARTICLES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to metal plating and more particularly to a process for the metal plating of an electrically nonconductive article or object on a plastisol-coated rack, usually a vinyl plastisol-coated rack, which eliminates any substantial deposition of metal on the rack. This invention also relates to a no rerack process for metal plating nonconductive articles or objects wherein the articles are retained on the same rack during the entirety of the process, and without the requirement of reracking the articles or objects on clean racks after the electroless metal plating and before the electroplating.

2. Description of the Prior Art

In the prior art the plastic articles or parts to be electrolessly metal plated were usually sensitized by immersion in a sensitizer solution, such as a stannous chloride-containing acid aqueous solution, prior to activating the articles. By reason of this sensitizing prior to activation, the insulating coating of the plastisol-coated plating racks, which was usually a vinyl polymer coating, also became metallized. This required reracking of the parts on clean racks prior to electroplating so as to prevent wasting of plating metal and to obtain proper plate distribution on the articles. However, the need to rerack the articles or parts on clean racks was time consuming and costly.

In an effort to prevent or inhibit electroless metal plating of the vinyl plastisol-coated racks the racks were treated heretofore in a chlorinated solvent, for instance trichloroethylene. However this resulted in severe and permanent damage to the plastisol coating.

Additional curing of the plastisol-coated racks to prevent metal plating thereof during the electroless metal plating may be effective for a few days after which the racks again are metal plated during the electroless plating. Further the danger of overcuring is attendant with the additional curing, with overcuring destroying desired physical properties of the plastisol of the rack coating.

OBJECTS OF THE INVENTION

A primary object of this invention is to provide a new and improved process for metal plating plastic articles or objects on plastisol coated racks otherwise susceptible to electroless metal plating deposition thereon, which eliminates the necessity of reracking the articles on clean racks after the electroless metal plating and prior to the electroplating.

Ancillary objects and advantages will be readily apparent as the invention is hereafter described.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that a electrically nonconductive article, object or part, for instance plastic articles, objects or parts, can be metal plated while racked on a plastisol-coated plating rack, usually a vinyl plastisol-coated rack without any substantial deposition of metal on the rack during the electroless plating step. This elimination of any substantial electroless deposition of metal on the rack which is otherwise susceptible to electroless plating deposition of metal thereon is accomplished in accordance with the invention by contacting the plastisol coated rack, prior to racking the electrically nonconductive article or articles destined to be metal plated thereon, with a liquid material such as a lower alkyl formamide, e.g. dimethylformamide, N-methyl-2-pyrrolidone, or a mixture of the lower alkyl formamide and N-methyl-2-pyrrolidone. Depending on the particular material or compound utilized for such contacting of the rack, the compound can be in liquid solution, for instance an aqueous solution of the compound, or the anhydrous compound per se. The contacting of the plating rack with such treatment liquid is effected for a time sufficient to render the plastisol-coated rack substantially nonsusceptible to the elec-

troless deposition of metal thereon during a subsequent chemical reduction metal plating step. The nonconductive article or articles or be plated are then racked on the thus-treated rack followed by activating the nonconductive article or articles and electrolessly metal plating the racked article by contacting the article with a chemical reduction metal plating solution until a metal plating of the desired thickness is deposited on the article surface, or until the article surface is rendered electrically conductive. This electroless metal plating of the racked article or articles occurs without any substantial metal plating of the rack. The thus-plated article or articles still on the same rack can then be and usually are electroplated, to deposit one or more metal electroplate layers over the electroless metal plate. By virtue of the contacting treatment of the rack with the alkyl formamide or N-methyl-2-pyrrolidone in accordance with this invention, there is eliminated the prior requirement of having to rerack the articles on clean racks after the electroless metal plating and prior to the electroplating. The vinyl polymer of the plastisol coating of the rack is usually polyvinyl chloride and the plastisol coating is over the structural members of the rack which are usually metallic structural members.

The contacting of the plating rack with the lower alkyl formamide or N-methyl-2-pyrrolidone is usually by immersing the rack in a liquid bath or pool of the anhydrous compound or a suitable solution thereof, usually an aqueous solution of the compound. However such contacting may be effected by spraying, pouring or in any other suitable manner. A contact time of the vinyl plastisol-coated rack with the preferred dimethylformamide herein of 1-2 minutes renders the rack immune or exempt from metal plating deposition for one complete plating cycle through the final electroplating step. Contact times of about 30-60 minutes of the vinyl plastisol-coated rack with dimethylformamide renders the rack immune or exempt from metal plating deposition for 24 hours and longer. With the longer contact times, there may be a slight swelling of the vinyl coating of the rack. Contact times of the vinyl plastisol-coated rack with N-methyl-2-pyrrolidone, also a preferred treating agent herein, for about 15-30 minutes renders the rack immune from electroless plating deposition of metal thereon for at least one complete plating cycle through the final electroplating step.

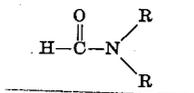
The present invention is primarily intended for use on plastisol-coated racks in an intermediate stage of their life and which have developed through use a susceptibility to plating metal thereon during the electroless plating step. This invention may not be advantageous for use on new plastisol-coated racks or on old racks inasmuch as such racks may not be susceptible to metal plating deposition during the electroless plating step. Of course if it is desired to use the present invention on new and old racks, this is considered within the invention's scope.

The contacting of the plastisol-coated rack with the liquid lower alkyl formamide and/or the liquid N-methyl-2-pyrrolidone can be carried out at room temperature, except when such compound is a solid in which event the solid is preheated into liquid form. During the contacting treatment of the rack, the liquified solid or liquid mixture containing same may be heated gently to maintain it in liquid phase.

When a mixture of the lower alkyl formamide and N-methyl-2-pyrrolidone is utilized herein to treat the plastisol-coated rack, the compounds can be employed in the liquid mixture in any desired suitable ratio. Whether such compounds are utilized in the mixture in anhydrous or substantially anhydrous state or in aqueous solution will be dependent on the particular lower alkyl formamide utilized. The preferred N, N-dimethylformamide and N-methyl-2-pyrrolidone are utilizable in the mixture in anhydrous or substantially anhydrous forms, or in aqueous formamide, both the N, N-diethyl formamide and N-methyl-2-pyrrolidone are utilized in anhydrous or substantially anhydrous form.

The lower alkyl formamide of this invention can usually be presented by the following formula:

3



wherein the R's each represent an alkyl group containing from one to four carbon atoms or a hydrogen atom with the proviso that at least one R is a 1-4C alkyl group. Examples of such carboxamides follow:

N-methylformamide
N, N-dimethylformamide
N-ethylformamide
N, N, N-diethylformamide
N-propylformamide
N, N, N-dipropylformamide
N-butylformamide
N, N-dibutylformamide

The lower alkyl formamides and N-methyl-2-pyrrolidone of this invention are readily obtainable in commerce.

The lower alkyl formamide can be utilized in anhydrous state or when in solution in a suitable liquid solvent, usually water. Aqueous solutions of N, N-dimethylformamide of about 58-95 weight percent dimethylformamide concentration are effective in inhibiting electroless metal plating of vinyl plastisol-coated racks. N, N-diethylformamide is effective in anhydrous or substantially anhydrous condition for inhibiting electroless metal plating of vinyl plastisol-coated racks. The N-methyl-2-pyrrolidone is also utilizable in the present invention in anhydrous or substantially anhydrous state or when in solution in a suitable liquid solvent, usually water. Thus aqueous solutions of N-methyl-2-pyrrolidone are effective for inhibiting electroless metal plating of vinyl plastisol-coated plating racks at concentrations of such compound of about 80 percent by weight and higher up to and including anhydrous state of the N-methyl-2-pyrrolidone.

Although the mechanism involved in the carboxamide treatment rendering the vinyl plastisol-coated rack nonsusceptible to the electroless deposition of metal thereon is not known with certainty, one plausible explanation advanced is that the lower alkyl formamide or N-methyl-2-pyrrolidone treatment results in a hardening and smoothing of the surface of the vinyl plastisol-coated rack to thereby prevent adherence of the activator catalyst particles and to prevent absorption of the stanous chloride sensitizer solution, when utilized.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred treatment compounds herein for rendering the plastisol-coated racks immune from electroless metal plating are the N, N-dimethyl formamide and N-methyl-2-pyrrolidone, utilized in the concentrations or state hereinbefore disclosed

The preferred mode of contacting the plastisol-coated rack with the lower alkyl formamide is by immersing the rack in a liquid bath or pool of the lower alkyl formamide or the N-methyl-2-pyrrolidone.

The following examples of carboxamide solutions, utilizable herein for treating the racks, further illustrate the invention but are not intended to be restrictive thereof:

EXAMPLE I

	% by Weight
N, N-dimethylformamide	91.7%
H ₂ O	8.3%

EXAMPLE II

N, N-dimethylformamide	94.7%
H ₂ O	5.3%

4

EXAMPLE III

N, N-dimethylformamide	85.8%
H ₂ O	14.2%

EXAMPLE IV

	% by Weight
N, N-dimethylformamide	80.9%
H ₂ O	19.1%

EXAMPLE V

N, N-dimethylformamide	75.2%
H ₂ O	24.8%

EXAMPLE VI

N, N-dimethylformamide	72.4%
H ₂ O	27.6%

EXAMPLE VII

N, N-dimethylformamide	68.9%
H ₂ O	31.3%

EXAMPLE VIII

N, N-dimethylformamide	63.5%
H ₂ O	36.5%

EXAMPLE IX

N, N-dimethylformamide	58.8%
H ₂ O	41.2%

EXAMPLE X

	% by Weight
N, N-dimethylformamide	94.7%
H ₂ O	5.3%

EXAMPLE XI

N-methyl-2-pyrrolidone	100%
H ₂ O	0%

EXAMPLE XII

N-methyl-2-pyrrolidone	80.4%
H ₂ O	19.6%

After the treatment of the vinyl plastisol-coated plating rack with the lower alkyl formamide or N-methyl-2-pyrrolidone in accordance with this invention is completed, the electrically nonconductive articles or parts to be plated, for instance plastic articles or parts, e.g. articles or parts of ABS copolymer, are racked on the thus-treated rack. The surfaces of the racked articles, if not already cleaned, are cleaned by immersion in a conventional nonsilicated alkaline cleaner solution. When the articles or parts have hydrophobic surfaces, which is usually the situation with plastic articles or parts, the surfaces are then converted from a hydrophobic state to a hydrophilic state wherein the surfaces are readily receptive to the aqueous solutions of the chemical reduction metal plating process or cycle. The conversion of the hydrophobic plastic surfaces to hydrophilic surfaces is preferably effected by contacting the hydrophobic surface with, usually by immersing such surfaces of the racked articles in, a conditioning or etchant solution comprising an aqueous acid solution containing concentrated sulfuric acid (typically of 98 percent H_2SO_4 concentration) and chromic acid (CrO_3), and which may also contain phosphate ions. The conversion of the hydrophobic article surfaces to hydrophilic surfaces can also be effected mechanically by roughening the hydrophobic surface, for instance by sanding, sand blasting or abrading the hydrophobic surface or surfaces. Exemplary of the conditioning solution is an aqueous solution of the following composition:

CrO_3	10 oz./gal.
H_2SO_4 (66 Be')	32 fl. oz./gal.

After conversion of the hydrophobic surfaces to hydrophilic surfaces is completed the articles still on the same rack are rinsed with water.

The hydrophilic nonconductive or nonmetallic surfaces of the racked articles are then activated in conventional manner, by contacting the hydrophilic surfaces with, usually by immersing the surfaces in, a sensitizer solution, usually a stannous chloride-containing aqueous acid solution containing, in addition to stannous chloride, HCl and water, followed by water rinsing. A typical sensitizer solution is the following:

$SnCl_2$	10 g.
HCl	40 ml.
H_2O	1,000 ml.

The HCl was the analytic reagent grade. The sensitizer is utilized at room temperature for 1-3 minutes.

The sensitized surfaces of the articles still on the same rack are then contacted with an activator solution, usually by immersing the surfaces in the activator solution. The activator solution is usually a palladous chloride-containing aqueous acid solution containing, in addition to palladous chloride, HCl and water. Other noble metal ions, e.g. platinum or gold ions, are utilizable in the activator solution instead of the ionic palladium. A typical activator solution has the following composition:

$PdCl_2$	1 g.
HCl	10 ml.
H_2O	1 gal.

The HCl was the analytic reagent grade. The above activator solution is used at room temperature, with one-half-1 minute immersion times. After activating is completed, the surface of the racked articles are then water rinsed.

Alternatively, the sensitizing step can be eliminated by combining the stannous chloride of the sensitizer and palladous chloride in one composition to form a colloidal catalyst solution containing colloidal palladium metal particles dispersed in a liquid medium as disclosed in U.S. Pat. No. 3,011,920. The racked plastic articles are immersed in or otherwise treated with the colloidal catalyst solution until their surfaces are activated for the subsequent electroless metal plating.

The racked activated articles are then electrolessly metal plated by contacting the article surfaces with, usually by immersing the articles in a chemical reduction metal plating solution in the usual manner. Exemplary of the chemical reduction metal plating solutions are chemical reduction copper plating solutions and chemical reduction nickel plating solutions or baths. The articles are maintained in contact with the chemical reduction metal plating solution until a metal layer of the desired thickness is deposited on the article surfaces, or until the article surfaces are rendered electrically conductive. Typical chemical reduction aqueous copper and nickel plating solutions follow:

CHEMICAL REDUCTION COPPER PLATING BATH

	g./l.
Copper sulfate	29
Sodium Carbonate	25
Rochelle salt	140
Versene T	17
Sodium hydroxide	40
Formaldehyde (37% solution)	166
Bath pH	11.5
Bath Temperature	70° F.

"Versene T" is a trademarked material containing EDTA and triethanolamine.

CHEMICAL REDUCTION NICKEL PLATING BATH

	g./l.
Nickel chloride	30
Sodium citrate	100
Ammonium chloride	50
Sodium hypophosphite	10
Adjust pH to pH 8-10 with NH_4OH	
Bath Temperature	190° F.

After the electroless metal plating is completed, the articles still on the same rack are then electroplated with, for example, copper in the usual manner. A typical electroplating bath for this purpose is an acid sulfate aqueous bath containing 200-300 g./l. of $CuSO_4 \cdot 5H_2O$ and 15-40 g./l. of free H_2SO_4 (66° Be'). After this electroplating step, one or more final electroplates, which may be decorative, are usually applied over the first-mentioned metal electroplate. These final electroplates are ordinarily thin layers and may be a layer of bright nickel followed by a layer of chromium thereover, or a layer of duplex nickel with a layer of microcracked chromium thereover.

The electrically nonconductive articles or parts metal plated herein include, for example, plastic knobs for window crank handles of automobiles and garnish or decorative plastic moldings for automobiles. The plastic includes, for example ABS copolymer, i.e. acrylonitrile-butadiene-styrene copolymer, and other polymers or plastics, e.g. polypropylene, polystyrene and polycarbonate.

In tests and experimental work conducted, N, N-dimethylformamide was found to inhibit electroless metal plating of the vinyl plastisol-coated plating rack after immersion of the rack in aqueous solutions of the N, N-dimethylformamide of about 58-95 weight percent N, N-dimethylformamide concentration. Aqueous solutions of higher concentration of the N, N-dimethylformamide than 95 percent and substantially anhydrous N, N-dimethylformamide, although inhibiting the electroless plating of the rack, attacked the polyvinyl chloride of the plastisol-coating of the rack. Substantially anhydrous N, N-diethylformamide was effective in inhibiting electroless metal plating of the vinyl plastisol-coated rack, but an aqueous solution of 80 percent by volume N, N-diethylformamide con-

centration was not effective in inhibiting the rack plating. Aqueous solutions of N-methyl-2-pyrrolidone of 80 volume percent and higher N-methyl-2-pyrrolidone concentration were found to be effective in inhibiting electroless metal plating of the vinyl plastisol-coated racks. Anhydrous N-methyl-2-pyrrolidone was also found to be effective in inhibiting electroless metal plating of such racks. However 2-pyrrolidone was not effective in anhydrous state or in aqueous solution of 95 volume percent 2-pyrrolidone concentration and actually enhanced electroless metal plating of the racks.

Formamide, acetamide and methyl ethyl ketone were found not effective for inhibiting electroless metal plating of vinyl plastisol-coated racks. Tetrahydrofuran was also found to be unsatisfactory for inhibiting such rack plating.

The tests also revealed that the N, N-dimethylformamide in aqueous solutions of the N, N-dimethylformamide concentration set forth immediately supra, the substantially anhydrous N, N-diethylformamide, the N-methyl-2-pyrrolidone in aqueous solutions of the N-methyl-2-pyrrolidone concentration set forth immediately supra, and anhydrous N-methyl-2-pyrrolidone, were effective in inhibiting electroless metal plating of the vinyl plastisol-coated racks when the activating was effected by immersing the racked plastic articles in a colloidal catalyst solution containing colloidal palladium metal particles dispersed in water. In the absence of the contacting of plastisol-coated racks with such compounds, the racks which were in an intermediate stage of life and susceptible to electroless metal plating were metal plated during the electroless plating step, when the activating was effected using the colloidal catalyst solution containing the colloidal palladium metal particles dispersed in water.

While the novel features of the invention have been disclosed herein and are specified in the annexed claims, it will be understood that various omissions, substitutions and changes may be made by those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. A process for the metal plating of electrically nonconductive articles on plastisol-coated plating racks, which comprises:

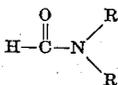
- a. contacting the plastisol-coated rack characterized by being susceptible to electroless metal plating, prior to racking thereon the electrically nonconductive articles destined to be plated, with a liquid material selected from the group consisting of a lower alkyl formamide, N-methyl-2-pyrrolidone, and mixtures thereof for a period sufficient to render the rack substantially non-susceptible to electroless plating of metal thereon during a subsequent chemical reduction metal plating step;
- b. racking at least one electrically nonconductive articles destined to be electrolessly metal plated on the thus-treated rack;
- c. activating hydrophilic surfaces of the racked nonconductive article; and
- d. electrolessly metal plating the racked activated article by contacting the article with a chemical reduction metal plating solution until a metal plating of a desired thickness is deposited on the article surface;
- e. the electroless metal plating of the racked article occurring without any substantial metal plating of the rack.

2. The process of claim 1 wherein the racked electrically nonconductive article is sensitized prior to being activated.

3. The process of claim 2 wherein the selected material is N, N-dimethylformamide.

4. The process of claim 2 wherein the selected material is N-methyl-2-pyrrolidone.

5. The process of claim 1 wherein the lower alkyl formamide is of the formula:



wherein the R's each represent a 1-4C alkyl group or a hydrogen atom with at least one R being a 1-4C alkyl group.

6. The process of claim 3 wherein the N,N-dimethylformamide is an aqueous solution of about 58-95 weight percent N,N-dimethylformamide concentration.

7. The process of claim 4 wherein the N-methyl-2-pyrrolidone is in an aqueous solution of at least about 80 weight percent N-methyl-2-pyrrolidone concentration.

8. A no rerack process for the metal plating of plastic articles on vinyl plastisol-coated racks, which comprises:

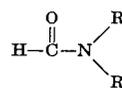
- a. contacting the vinyl plastisol-coated rack characterized by being susceptible to electroless metal plating, prior to racking the plastic articles destined to be plated, with a liquid material selected from the group consisting of a lower alkyl formamide, N-methyl-2-pyrrolidone, and mixtures thereof, for a period sufficient to render the rack substantially non-susceptible to electroless plating of metal thereon during a subsequent chemical reduction metal plating step;
- b. racking plastic articles destined to be metal plated on the thus-treated rack;
- c. converting hydrophobic surfaces of the racked plastic articles to hydrophilic surfaces receptive to chemical reduction metal plating process aqueous solutions;
- d. activating the hydrophilic surfaces of the racked plastic articles;
- e. electrolessly metal plating the racked activated plastic article surfaces by contacting the articles with a chemical reduction metal plating solution until the article surfaces are rendered electrically conductive; and
- f. without reracking the electrolessly metal plated article, electroplating a metal layer onto the conductive surface of the articles while still on the same rack;
- g. the electroless metal plating of step (e) and hence the electroplating of step (f) occurring without any substantial metal plating of the rack.

9. The process of claim 8 wherein the racked plastic articles are sensitized prior to being activated.

10. The process of claim 9 wherein the selected material is N,N-dimethylformamide.

11. The process of claim 9 wherein the selected material is N-methyl-2-pyrrolidone.

12. The process of claim 8 wherein the lower alkyl formamide is of the formula



wherein the R's represent a 1-4C alkyl group or a hydrogen atom with at least one R being a 1-4C alkyl group.

13. The process of claim 9 wherein the electroless metal plating is electroless copper plating and the chemical reduction metal plating solution is a chemical reduction copper plating solution.

14. The process of claim 9 wherein the electroless metal plating is electroless nickel plating and the chemical reduction metal plating solution is a chemical reduction nickel plating solution.

15. The process of claim 9 wherein the contacting of the rack with the selected liquid material is effected by immersing the rack in a liquid bath thereof.

16. The process of claim 10 wherein the N,N-dimethylformamide is in an aqueous solution of about 58-95 weight N,N-dimethylformamide concentration.

17. The process of claim 11 wherein the N-methyl-2-pyrrolidone is in an aqueous solution of at least about 80 weight percent N-methyl-2-pyrrolidone concentration.

18. The process of claim 8 wherein the hydrophobic surfaces of the racked plastic articles are converted to the hydrophilic surfaces by immersing the racked articles in a conditioning solution comprising an aqueous acid solution containing

9

10

concentrated sulfuric acid and chromic acid for a period sufficient to effect such conversion.

19. The process of claim 8 wherein the electroplating of the racked articles is of a copper electroplate layer onto the conductive surfaces thereof.

20. The process of claim 19 further characterized by electroplating one or more final metal electroplate layers over the copper electroplate layer while the articles are still on the same rack.

21. A preconditioned vinyl plastisol-coated rack for holding articles destined to be metal plated and characterized by being substantially nonsusceptible to electroless plating deposition of metal thereon while immersed in a chemical reduction

metal plating solution, the rack having been conditioned by contacting the same with a liquid material selected from the group consisting of N,N-dimethylformamide, N-methyl-2-pyrrolidone, and mixtures thereof for a time sufficient to render the rack substantially nonsusceptible to electroless plating deposition of metal thereon while in contact with the chemical reduction metal plating solution.

22. The rack of claim 21 wherein the selected material is N,N-dimethylformamide.

23. The rack of claim 21 wherein the selected material is N-methyl-2-pyrrolidone.

* * * * *

15

20

25

30

35

40

45

50

55

60

65

70

75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,243 Dated November 9, 1971

Inventor(s) Frank A. Brindisi, Jr. and Theophil J. Wiczorek

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 8, "articles" should read --article--.
Column 2, line 3, "or" (second occurrence) should read --to--;
line 10, after "ing" the letter --o-- should be deleted; line 70,
after "aqueous" --formamide-- should be deleted and the following
should be inserted after "aqueous" and before "both" --solution.
When the lower alkyl formamide is N,N-diethylformamide,--; line
74, "presented" should read --represented--. Column 3, line 13,
"N,N,N-diethylformamide" should read --N,N-diethylformamide--;
line 15, "N,N,N-dipropylformamide" should read --N,N-dipropylforma-
mide--. Column 4, line 36, "31.3%" should read --31.1%--; line
58, "N,N-dimethylformamide" should read --N,N-diethylformamide--.
Column 7, line 52, "articles" should read --article--.

Signed and sealed this 16th day of May 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents