

[54] **TREATING SOLUTION FOR
PLANOGRAPHIC PRINTING PLATES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 814,792, April 9, 1969, abandoned.

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[58] Field of Search. **106/219-232, 286; 101/450-467; 117/47, 135.5, 169, 36.8, 36.9, 127; 96/1, 1.5, 1.6, 49, 62, 92; 148/6.15**

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A treating solution for planographic printing plates, which consists essentially of an aqueous solution containing dissolved therein at least one iron-cyano-complex such as ammonium ferrocyanide, sodium ferrocyanide, sodium ferricyanide, potassium ferrocyanide and potassium ferricyanide, at least one heteropoly-acid such as phosphorus vanadate and ammonium or alkali metal salts of said acids and at least one phosphate such as diammonium hydrogen phosphate, sodium dihydrogen phosphate and dipotassium hydrogen phosphate, the balance, apart from impurities, being water.

4 Claims, No Drawings

TREATING SOLUTION FOR PLANOGRAPHIC PRINTING PLATES

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 814,792, filed Apr. 9, 1969, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a hydrophilic treating solution for use in offset printing for the purpose of making hydrophilic the non-image areas of both offset printing plates having a paper support and offset type planographic printing plates having a metal or plastic or other support. The hydrophilic treating solution referred to in this invention also involves what is called a fountain solution for use in offset printing which is obtained by diluting the aforementioned treating solution.

2. Description of the Prior Art

Offset type planographic printing plates have been widely developed under various types and so have many kinds of compositions to make their plate materials. For instance, when an offset printing plate is utilized in which the image is produced by electrophotography, a layer consisting of a resin binder dispersed with zinc oxide is formed over the surface of a support when a printing plate is utilized in which an image is produced on the surface of its support by means of xerography and a printing plate is utilized in which an image is produced directly on its support, a layer consisting of a hydrophilic colloidal matter, clay, etc. is formed on the surface of a support and the layer is set up for hardening by submitting same to an after-treatment with an aqueous solution which contains metallic salts. Such plates that are prepared by forming a diazotype light-sensitive layer upon the surface of a support such as paper, metal plate and plastic sheet treated with aforementioned hardening set up are also widely known. It is generally believed that if the materials which compose the surface of printing plates are different treating solutions should be used in order to make the non-image areas on the surfaces of said printing plates hydrophilic depending on the type of the respective layer composition used in preparing the printing plates. At the present, there are commercially available various types of treating solutions for planographic printing plates having special formulations in order to function effectively with the compositions of the surfaces of the respective types of printing plates.

However, when several types of printing plates made of different materials are to be used for printing on one offset type planographic printing machine, the treating solutions have to be changed, much to the inconvenience of the users, so that the succeeding treating solution will meet the requirements of the succeeding printing plate.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a universal type treating solution for planographic printing plates made that can be used for making hydrophilic the aforementioned printing plates of various types of materials. Therefore, when the treating solution which is prepared according to the present invention is used in offset printing, it completely avoids the necessity of changing the treating solutions, which has

been a conventional practice followed when a printing plate of different type from the previous one is to be used on the printing machine.

The inventors have successfully accomplished the object of this invention by finding that a treating solution consisting essentially of an aqueous solution containing three components i.e., heteropoly-acid, iron-cyano-complex and phosphate, has general purpose performances. The invention is the result of experimental research work in which various types of compositions were prepared to make treating solutions of many kinds and determining how successfully each of them coact with the respective printing plates that are made of different kinds of materials.

A treating solution according to the present invention should accordingly contain the following three components in order to make hydrophilic the non-image areas on the surface of said printing plates made of various types of plate materials.

As for the first of the indispensable components, namely, iron-cyano-complex, iron-cyano-complexes of ammonium and iron-cyano-complexes of alkali metals are best suited for the purpose and, for instance, ammonium ferrocyanide, ammonium ferricyanide, sodium ferrocyanide, sodium ferricyanide, potassium ferrocyanide and potassium ferricyanide are used.

As for the second of said components, namely, heteropoly-acid, there are used any of such heteropoly acids that are water soluble and contain water of crystallization in large quantities and are stable enough not to be decomposed in an acid solution. For instance, heteropoly-acids such as phosphomolybdic phosphotungsted and phosphovanadic acids are suitable for the purpose. In this invention, these heteropoly-acids can be used as salts of alkali metals such as sodium and potassium, or ammonium salts. Also, sodium molybdate and sodium tungstate can be used. Furthermore, salts which are expressed by the general formula such as $2(M^1)_2O \cdot P_2O_5 \cdot 5MoO_3 \cdot nH_2O$ (wherein, M^1 is selected from the group consisting of Na, K and NH_4 , and n is whole number in the range of 2-22), are applicable in this invention. These heteropoly-acids have a property to solidify proteins such as gelatin, casein and albumen. A treating solution which contains any of these heteropoly-acids, therefore, when used for plate materials which have a printing surface containing a protein, not only increases the strength of the layer physically as well as mechanically but also improves its printing quality and lengthens its printing life, and also contributes to give the image-areas formed on the plate surface a water-repellent property.

As for phosphates, the third of said components, all phosphates are usable for the present invention so far as they are water soluble; however, alkali metal salts and ammonium salts such as disodium hydrogen phosphate, sodium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium dihydrogen phosphate, diammonium hydrogen phosphate, and ammonium dihydrogen phosphate are the most suitable ones.

The treating solutions according to the present invention contain from about 0.5 to about 20 percent by weight of at least one iron-cyano-complex selected from among the aforementioned various kinds of iron-cyano-complexes, from about 0.05 to about 10 percent by weight of at least one heteropoly-acid selected from among the heteropoly-acids and from about 1.0 to about 20 percent by weight of at least one phosphate

selected from among the phosphates, the balance, apart from impurities, being water. In addition to the aforementioned three components, it is advisable in the present invention to use at least one compound selected from among such hydrophilic colloidal materials as gum arabic, sodium alginate, ester of alginic acid and propylene glycol, propylene glycol, carboxymethyl cellulose, dextrin, polyacrylic acid and glycerine.

Therefore, the present invention is also featured in providing a treating solution consisting essentially of an aqueous solution containing the three components i.e., iron-cyano-complex, heteropoly-acid and phosphates, and from about 1.0 to about 20 percent by weight of at least one hydrophilic colloidal material selected from among the aforementioned hydrophilic colloidal materials.

It is important that the concentration of each of the components is within the specified ranges, one or other of the desired properties falling off if the concentration of any of them is outside the limits set forth above.

When the concentration of each of iron-cyano-complex and heteropoly-acid in the treating solution is in excess of the respective maximum of the aforementioned ranges, it tends to bring about the defect that the printing ink is absorbed even onto the non-image areas outside the image areas of the printing plate, while when the concentration is below the minimum of said range, it tends to bring about the defect that a sufficient quantity of printing ink is hardly absorbed onto the image areas of the printing plate.

The concentration of the phosphate in the treating solution must also be within said range, and when the phosphate concentration above the maximum of said range is used, it tends to bring about the defect that a sufficient quantity of printing ink is hardly adsorbed onto the image areas of printing plate, while when the concentration is below the minimum of said range, it tends to bring about the defect that the printing ink is adsorbed even onto the non-image areas outside the image areas of printing plate.

The hydrophilic colloidal materials in the present invention contribute greatly to the improvement of the hydrophilic effect of the treating solution.

When the concentration of hydrophilic colloidal materials in the treating solution is less than 1.0 percent, the effect resulting from the addition of such materials is limited only to an extremely small extent. In other words, since the treating solution according to the present invention per se possesses, without containing such materials, a function enough to make the non-image areas hydrophilic, it is difficult to observe an effect to be brought about by addition of small amounts of these materials. When the contents of such materials in the treating solution are more than 20 percent, on the other hand, there can be observed a tendency to cause insufficient adhesion of ink to the image areas.

Taking into consideration the relation between the concentration and the effect of the respective components as aforesaid, it will be most preferable in the present invention that the concentration of each component lies within the range as given below.

Iron-cyano-complex: from about 0.5 to about 10 percent by weight

Heteropoly-acid: from about 0.05 to about 5 percent by weight

Phosphate: from about 1.0 to about 10 percent by weight

Hydrophilic colloidal material: from about 1.0 to about 10 percent by weight

When a treating solution composed of the aforementioned components according to this invention is used to treat printing plates, it can be used to make hydrophilic printing plates of various types of plate materials and in printing, the printing ink shows a good lay and satisfactory printing results can be obtained from the very beginning of the printing. While heightening the hydrophilic effect of the non-image area of printing plates, the treating solution improves the water-repellent property of the image areas, and also improves the lay of ink in the solid areas, which problem has heretofore been encountered in case of offset printing plates prepared by electrophotography, and possesses the advantage of improving the printing quality of the plates. Other merits are that this treating solution and a fountain solution prepared by diluting this treating solution can be used satisfactorily on the offset press equipped with an automatic etching device, and that since it is not necessary to change the treating solution even when the printing plates are changed, this treating solution contributes much to the saving of time in printing operations.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will be further illustrated by the following examples:

Example 1

A reproduced image was formed according to a usual method on a commercially available electrophotographic copying paper (which is prepared by forming a photoconductive layer having the thickness of 10 μ consisting of acrylic resin which contains zinc oxide on the surface of a paper support having water resisting qualities) and then the image area was fixed by heating. After that,

phosphotungstic acid	1 part by weight
(hydrogen phosphorus wolframate)	50 parts by weight
ammonium dihydrogen phosphate	50 parts by weight
sodium ferrocyanide	

were dissolved in water. Water was further added to this solution until a total of 1,000 parts by weight of an aqueous solution was obtained as a treating solution for use in offset printing, and part of the treating solution was diluted in water at the ratio of 1:10 to prepare a fountain solution. The aforementioned image carrying copying paper was made hydrophilic by the use of the treating solution, and then was set on the offset press to conduct printing while wetting the image carrying copying paper with said fountain solution. More than 3,000 copies of prints carrying a clearly printed image were obtained and the lay of ink was very good from the beginning of the printing.

Example 2

After a plate material of copying paper carrying an image obtained according to Example 1 was treated with a solvent steam of trichlene to fix the said image, the plate surface was treated with a treating solution comprising the undermentioned components and set for the printing. Two thousand copies of prints carrying a clear image were thus obtained. Water was added to

phosphomolybdic acid	2 parts by weight
(hydrogen phosphorus molybdate)	30 parts by weight
disodium hydrogen phosphate	40 parts by weight
potassium ferricyanide	

glycerine

50 parts by weight

to make the total quantity of 1,000 parts by weight.
Example 3

A solution consisting of 100 parts by weight of 3% aqueous solution of sodium carboxymethyl cellulose having a low viscosity, 20 parts by weight of colloidal silica, 20 parts by weight of clay and 20 parts by weight of glycerine was coated on a paper support having water resisting properties. In order to make the coating layer insoluble, it was further treated with a 5% aqueous solution consisting of copper sulfate and aluminum sulfate, and was then dried to make a plate material for use in direct image writing. After having an image drawn on the surface of this plate material by the use of an oily pencil (typewriter or electrostatic reproduction may also be used), the plate material was treated with a treating solution comprising the undermentioned components to make it hydrophilic:

phosphotungstic acid (hydrogen phosphorus wolframate)	5 parts by weight
potassium hydrogen phosphate	30 parts by weight
sodium ferrocyanide	10 parts by weight
carboxymethyl cellulose	5 parts by weight
glycerine	200 parts by weight

to which water was added to make the total quantity of 1,000 parts by weight of aqueous solution. When offset type planographic printing was conducted using said plate material, 3,000 copies of prints having a clearly printed image thereon were obtained. The lay of the ink on the plate was very good. As for a fountain solution, part of the treating solution having the abovementioned components was used after it was diluted with water at the ratio of 1:20.

Example 4

A solution comprising the following components was applied to the surface of paper support having water resisting properties:

hydroxy ethyl cellulose	5 parts by weight
polyvinyl alcohol	5 parts by weight
aluminum hydroxide	20 parts by weight
dimethylol melamine	1 part by weight
ammonium chloride	0.5 part by weight
water	200 parts by weight

The plate thus obtained was hot-set to make a plate material for use in direct image writing, upon which an image was drawn with a ball-point pen. The plate was then treated with a treating solution consisting of the following components:

phosphomolybdic acid (hydrogen phosphorus molybdate)	0.5 part by weight
sodium dihydrogen phosphate	50 parts by weight
sodium ferricyanide	30 parts by weight
sodium alginate	10 parts by weight
glycerine	50 parts by weight

to which water was added to make the total quantity of 1,000 parts by weight. When the plate was set on the offset press of for printing it demonstrated the same printing properties and performances as that of Example 3.

Example 5

After having been removed of grease, an aluminum foil having a thickness of 0.1 mm was treated with an aqueous solution of polyacrylic acid and then an offset sensitive solution containing diazo resin (solution is composed of 5 g. of diazo-benzenesulfonic acid, 1 g. of denatured vinyl acetate resin, 60 ml of acetone, and 50 ml of dioxane) was applied to the surface of the alumi-

num foil in order to form a negative type sensitive layer thereby to prepare a plate material.

A negative original was placed on the plate material, exposed to ultraviolet rays, developed and made hydrophilic simultaneously with a treating solution composed of the following components:

phosphotungstic acid (hydrogen phosphorus wolframate)	1 part by weight
sodium ferrocyanide	5 parts by weight
diammonium hydrogen phosphate	20 parts by weight
sodium alginate	5 parts by weight
ethylene glycol	100 parts by weight

to which water was added to make the total quantity of 1,000 parts by weight. The performance of the abovementioned treating solution was approximately equal to those treating solutions referred to in Examples 1-4.

Example 6

A solution of methyl cellosolve containing diazo compounds (for instance, ester of naphthoquinone-(1, 2)-diazido sulfonic acid) of quinone diazido type was applied to the surface of a paper support having water resisting qualities and was dried, on which a positive original was placed and exposed to ultraviolet rays for three minutes. The plate was developed with an alkaline developer, was also fixed and made hydrophilic by the use of a treating solution which was composed of the following components:

phosphomolybdic acid (hydrogen phosphorus molybdate)	10 parts by weight
ammonium hydrogen phosphate	50 parts by weight
potassium ferricyanide	5 parts by weight
ester of alginic acid-propylene glycol	20 parts by weight
propylene glycol	100 parts by weight

to which water was added to make the total quantity of 1,000 parts by weight.

Example 7

Treating solutions having the components as shown in Table 1 were prepared.

TABLE 1

Treating Solution No.	Iron-cyano Complex (Parts by weight)	Heteropoly-acid (parts by weight)	Phosphate (Parts by weight)	Water (parts by weight)
40	Potassium ferricyanide (5)	Phosphorus molybdate $[2Na_2O \cdot P_2O_5 \cdot 5MoO_3 \cdot nH_2O]$ (2)	Ammonium dihydrogen phosphate (5)	
45	Sodium ferrocyanide (5)	Phosphorus molybdate $[2(NH_4)_2O \cdot P_2O_5 \cdot 5MoO_3 \cdot nH_2O]$ (1)	Potassium dihydrogen phosphate (5)	978
50	Sodium ferrocyanide (5)	Sodium molybdate $[Na_2MoO_4 \cdot 2H_2O]$ (5)	Ammonium dihydrogen phosphate (7)	
55	Ammonium ferrocyanide (5)		Diammonium hydrogen phosphate (3)	975
60	Sodium ferrocyanide (10)	Sodium molybdate $[Na_2MoO_4 \cdot 2H_2O]$ (2)	Ammonium dihydrogen phosphate (5)	976

7

Sodium
wolframate
[Na₂WO₄·2H₂O]
(1)

Sodium
dihydrogen
phosphate
(5)

It was confirmed that the properties and performances of these treating solutions were as same as those of the treating solutions given in the foregoing Examples.

Example 8

The printing plates used in aforesaid Examples were respectively made hydrophilic with treating solutions having undermentioned compositions. As a result, it was recognized that said treating solutions possess the same effect as those used in the Examples.

Treating solution No. 1	
Sodium ferrocyanide	5 parts by weight
Phosphotungstic acid	100 parts by weight
Sodium hydrogen phosphate	200 parts by weight
Water	695 parts by weight
Treating solution No. 2	
Sodium ferrocyanide	3 parts by weight
Sodium ferrocyanide	2 parts by weight
Phosphomolybdic acid	10 parts by weight
Sodium dihydrogen phosphate	200 parts by weight
Water	785 parts by weight
Treating solution No. 3	
Potassium ferrocyanide	5 parts by weight
Disodium phosphorus molybdate [2Na ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	0.5 part by weight
Dipotassium hydrogen phosphate	10 parts by weight
Water	984.5 parts by weight
Treating solution No. 4	
Potassium ferrocyanide	5 parts by weight
Diammonium phosphorus molybdate [2(NH ₄) ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	5 parts by weight
Potassium dihydrogen phosphate	10 parts by weight
Water	980 parts by weight
Treating solution No. 5	
Potassium ferrocyanide	50 parts by weight
Ammonium ferrocyanide	100 parts by weight
Sodium ferrocyanide	50 parts by weight
Phosphotungstic acid	50 parts by weight
Sodium molybdate [Na ₂ MoO ₄ ·2H ₂ O]	50 parts by weight
Diammonium hydrogen phosphate	100 parts by weight
Disodium hydrogen phosphate	100 parts by weight
Water	500 parts by weight
Treating solution No. 6	
Ammonium ferrocyanide	150 parts by weight
Phosphomolybdic acid	50 parts by weight
Sodium wolframate	20 parts by weight
Ammonium dihydrogen phosphate	10 parts by weight
Water	770 parts by weight
Treating solution No. 7	
Ammonium ferrocyanide	100 parts by weight
Ammonium ferrocyanide	100 parts by weight
Diammonium phosphorus molybdate [2(NH ₄) ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	0.5 part by weight
Ammonium dihydrogen phosphate	100 parts by weight
Water	699.5 parts by weight
Treating solution No. 8	
Potassium ferrocyanide	200 parts by weight
Disodium phosphorus molybdate [2Na ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	1 part by weight
Sodium dihydrogen phosphate	200 parts by weight
Water	599 parts by weight
Treating solution No. 9	
Sodium ferrocyanide	100 parts by weight
Phosphomolybdic acid	10 parts by weight
Ammonium dihydrogen phosphate	100 parts by weight
Water	790 parts by weight
Treating solution No. 10	
Sodium ferrocyanide	5 parts by weight
Phosphotungstic acid	50 parts by weight
Disodium hydrogen phosphate	100 parts by weight
Gum arabic	100 parts by weight
Water	745 parts by weight
Treating solution No. 11	
Sodium ferrocyanide	100 parts by weight
Phosphomolybdic acid	0.5 part by weight
Sodium dihydrogen phosphate	100 parts by weight
Sodium alginate	50 parts by weight
Gum arabic	50 parts by weight
Water	699.5 parts by weight
Treating solution No. 12	
Potassium ferrocyanide	50 parts by weight
Potassium ferrocyanide	50 parts by weight

8

Disodium phosphorus molybdate [2Na ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	10 parts by weight
Dipotassium hydrogen phosphate	10 parts by weight
Propylene glycol	100 parts by weight
Water	780 parts by weight
Treating solution No. 13	
Potassium ferricyanide	5 parts by weight
Diammonium phosphorus molybdate [2(NH ₄) ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	0.5 part by weight
Potassium dihydrogen phosphate	10 parts by weight
Carboxymethyl cellulose	10 parts by weight
Water	974.5 parts by weight
Treating solution No. 14	
Ammonium ferrocyanide	100 parts by weight
Phosphotungstic acid	30 parts by weight
Sodium molybdate [Na ₂ MoO ₄ ·2H ₂ O]	20 parts by weight
Diammonium hydrogen phosphate	100 parts by weight
Dextrin	10 parts by weight
Water	740 parts by weight
Treating solution No. 15	
Ammonium ferricyanide	100 parts by weight
Phosphotungstic acid	10 parts by weight
Phosphomolybdic acid	10 parts by weight
Sodium wolframate	10 parts by weight
Sodium dihydrogen phosphate	50 parts by weight
Ammonium dihydrogen phosphate	50 parts by weight
Polyacrylic acid	100 parts by weight
Water	670 parts by weight
Treating solution No. 16	
Ammonium ferricyanide	100 parts by weight
Diammonium phosphorus molybdate [2(NH ₄) ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	0.5 part by weight
Ammonium dihydrogen phosphate	10 parts by weight
Glycerine	10 parts by weight
Water	879.5 parts by weight
Treating solution No. 17	
Potassium ferricyanide	5 parts by weight
Disodium phosphorus molybdate [2Na ₂ O·P ₂ O ₅ ·5MoO ₃ ·nH ₂ O]	30 parts by weight
Sodium dihydrogen phosphate	10 parts by weight
Gum arabic	10 parts by weight
Water	945 parts by weight
Treating solution No. 18	
Sodium ferrocyanide	5 parts by weight
Sodium ferrocyanide	5 parts by weight
Phosphomolybdic acid	1 part by weight
Dipotassium hydrogen phosphate	20 parts by weight
Ammonium dihydrogen phosphate	60 parts by weight
Sodium dihydrogen phosphate	20 parts by weight
Sodium alginate	10 parts by weight
Water	879 parts by weight
Treating solution No. 19	
Sodium ferrocyanide	10 parts by weight
Phosphotungstic acid	10 parts by weight
Disodium hydrogen phosphate	10 parts by weight
Gum arabic	20 parts by weight
Propylene glycol	60 parts by weight
Carboxymethyl cellulose	20 parts by weight
Water	870 parts by weight

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A treating solution for planographic printing plates, which consists essentially of an aqueous solution of (a) from about 0.5 to about 20 percent by weight of at least one iron-cyano-complex selected from the group consisting of sodium ferrocyanide, sodium ferricyanide, potassium ferrocyanide, potassium ferricyanide, ammonium ferricyanide and ammonium ferrocyanide, (b) from about 0.05 to about 10 percent by weight of at least one material selected from the group consisting of phosphomolybdic acid, phosphotungstic acid, phosphovanadic acid, ammonium salts of said acids, alkali metal salts of said acids, sodium molybdate and sodium tungstate, and (c) from about 1.0 to about 20 percent by weight of at least one phosphosphate selected from the group consisting of disodium hydrogen phosphate, sodium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium dihydrogen phosphate, the balance of said solution, apart from impurities, being water.

2. A treating solution according to claim 1, wherein the concentration of said iron-cyano-complex is in the range of from about 0.5 to about 10 percent by weight, the concentration of said material (b) is in the range of from about 0.05 to about 5 percent by weight, and the concentration of said phosphate is in the range of from about 1.0 to about 10 percent by weight.

3. A treating solution for planographic printing plates, which consists essentially of an aqueous solution of (a) from about 0.5 to about 20 percent by weight of at least one iron-cyano-complex selected from the group consisting of sodium ferrocyanide, sodium ferricyanide, potassium ferrocyanide, potassium ferricyanide, ammonium ferricyanide and ammonium ferrocyanide, (b) from about 0.05 to about 10 percent by weight of at least one material selected from the group consisting of phosphomolybdic acid, phosphotungstic acid, phosphovanadic acid, ammonium salts of said acids, alkali metal salts of said acids, sodium molybdate and sodium tungstate, (c) from about 1.0 to about 20 percent by weight of at least one phosphate selected

from the group consisting of disodium hydrogen phosphate, sodium di-hydrogen phosphate, dipotassium hydrogen phosphate, potassium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and (d) from about 1.0 to about 20 percent by weight of at least one compound selected from the group consisting of gum arabic, sodium alginate, ester of alginic acid-propylene glycol, propylene glycol, carboxymethyl cellulose, dextrin, polyacrylic acid and glycerine, the balance of said solution, apart from impurities, being water.

4. A treating solution according to claim 3, wherein the concentration of said iron-cyano-complex is in the range of from about 0.5 to about 10 percent by weight, the concentration of said material (b) is in the range of from about 0.05 to about 5 percent by weight, the concentration of said phosphate is in the range of from about 1.0 to about 10 percent by weight, and the concentration of said compound is in the range of from about 1.0 to about 10 percent by weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3 769 043

Dated October 30, 1973

Inventor(s) Tsuyoshi Morishima and Rentaro Shimizu

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

On the Title Page insert Priority Data as below:

"Claims Priority Japan Serial No. 24 649 filed
April 13, 1968."

Col. 8, line 62; change "phosophate" to ---phosphate---

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

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Commissioner of Patents