ABSTRACT OF THE DISCLOSURE

A method for applying a zinc phosphate coating to a metallic surface by contacting the surface with an aqueous phosphatizing solution which initially contains phosphate, zinc and nitrate ions in a ratio of

$$P_2O_5:Zn(NO_3) = 1:(1.4 \text{ to } 2.6):(2.0 \text{ to } 4.3)$$

replenishing the solution, as needed, by adding thereto phosphate, zinc and nitrate ions in a ratio of

$$P_2O_5:Zn(NO_3) = 1:(0.40 \text{ to } 0.53):(0.45 \text{ to } 0.70)$$

establishing in the solution at the beginning of the coating cycle a nitrate concentration of at least 0.01%, nitrate being maintained in the solution throughout the coating cycle by autowarming generation thereof, the solution also containing a metallic accelerator selected from the group consisting of copper, nickel and cobalt and mixtures thereof.

This invention concerns improvements in or relating to processes for the production of zinc phosphate coatings.

It is already conventional to produce zinc phosphate coatings on workpieces of iron, steel, zinc, cadmium and their alloys by means of a process which employs a weakly acidic aqueous solution of primary zinc phosphate, possibly also containing nitrates.

During the phosphatizing process insoluble tertiary zinc phosphate is deposited on the metal surface in the form of a coating, while iron is simultaneously dissolved off any iron-containing metal surface and enters the solution in the divalent ferrous form. It is however desirable to keep the phosphatizing solution substantially iron-free, in order to obtain good corrosion-resistant and firmly adherent phosphate coatings. The phosphatizing solution is therefore conventionally kept practically free from dissolved iron by the addition of an alkali-metal nitrate such as sodium nitrate or potassium nitrate. This nitrite converts the dissolved iron from the divalent ferrous form into the trivalent ferric form, since tertiary ferric phosphate is only slightly soluble in acid phosphatizing baths the dissolved iron is thus precipitated out of the solution as sludge, provided that one can maintain a sufficient concentration of nitrite or nitrous acid in the bath. The alkali-metal nitrate also serves simultaneously as an accelerator for the phosphatizing process. However, since the alkali-metal nitrates and also the free nitrous acid which is formed therefrom in acid phosphatizing baths are both quickly broken down at the conventional phosphatizing temperatures of 60–80°C, it is necessary in this conventional procedure to add the alkali-metal nitrite to the phosphatizing solution very frequently or even continuously, normally in small quantities such that a slight excess of about 0.0005–0.005% of NO$_3$ is always maintained therein.

The zinc and phosphate consumed in this conventional type of phosphatizing process are replaced, continuously or intermittently by adding a sufficient amount of replenishment materials containing them to restore the point number or pointage of the solution, since these known phosphatizing solutions only produce coatings with optimum properties when maintained at a definite pointage.

In one particular known version of this process the solution, which contains a coating-forming mono-phosphate such as for example zinc phosphate as well as zinc nitrate, is replenished simultaneously not only with the standard replenishment materials indicated above but also with another acid which can form sodium nitrate with the sodium of the continuously-added sodium nitrite. Such another acid can clearly be nitric acid, which therefore is added in such an amount as will suffice for the neutralization of the sodium introduced originally as sodium nitrite.

In another known version of the conventional process, the composition of the zinc phosphate solution is held constant with respect to P$_2$O$_5$ and zinc, by using solutions which contain P$_2$O$_5$, zinc, NO$_3$, NO$_2$ and alkali-metal ions in a ratio of

$$P_2O_5:Zn(NO_3):NO_2 = 1:(0.48–0.53):(0.53–0.26)$$

and continuously replenishing them with a replenishment material containing P$_2$O$_5$, NO$_3$, zinc and alkali-metal nitrite in a ratio of

$$P_2O_5:Zn(NO_3):NO_2 = 1:(0.48–0.53):(0.53–0.26):(0.31–0.22)$$

in such a manner as to restore the P$_2$O$_5$ content to its original value. Thus, in this process, after determination of the point number, replenishment must be carried out continuously, not only with a solution which contains P$_2$O$_5$, zinc and NO$_3$ but also separately with an alkali-metal nitrite in a quite definite quantity ratio. Within the limits laid down for this known process the individual components are selected in such a way that with a rising zinc content the nitrate and nitrite content falls, that is, for example, drops to one part P$_2$O$_5$, 0.48 part zinc, 0.53 part NO$_3$ and 0.31 part NO$_2$ or to one part P$_2$O$_5$, 0.53 part zinc, 0.26 part NO$_3$ and 0.22 part NO$_2$.

It is also known that in a zinc phosphate bath, which contains primary zinc phosphate and zinc nitrate, preferably but optionally together with sodium nitrate, it is possible by increasing the ratio of NO$_3$:P$_2$O$_5$ until it is at least 1:1 and preferably greater, for example 2:1 to 4:1, for nitrite to be formed automatically by breakdown of the nitrate, in an amount sufficient to catalyse the precipitation of the iron and for acceleration of the phosphatizing process, so that it is then unnecessary to add nitrite to the solution continuously. Instead, at the beginning of the work (or possibly intermittently during phosphatizing) there is added a small quantity of sodium nitrite corresponding to 0.002% NO$_3$—the nitrite content should thereafter be maintained by the autocatalytic formation of nitric acid, and it can build up in the solution as high as 0.01% NO$_3$. In this procedure however, the autocatalytic formation of nitric acid occurs only if the solution has both a high point number and a high temperature of preferably 82°C.

There also exists another known process in which the autocatalytic formation of NO$_3$ from nitrates can take place—the solutions employed contain 1–1.5% NO$_3$ at least 0.045% zinc and at least 0.5% P$_2$O$_5$ while they have an acid ratio of at least 1:5.3 and a pH value of 2–2.5. In these solutions more than half of the zinc is combined with phosphate, and they can only operate at low concentrations and low pointages of about 20. However, the nitrite concentration in the solution should be at least 0.0005% NO$_3$, and in this process the nitrite formation takes place very slowly and to an insufficient extent, so that it is necessary to restrict the process to very small
bath loadings such that not more than 60 cm.² of metal surface to be treated shall ever be present per litre of the solution.

It has now been found that by radically altering certain quantitative ratios and in particular by combining a very large proportion of the zinc with nitrate rather than phosphate, it is possible under prescribed working conditions, to generate nitrite autocatalytically in quantities sufficiently great even for rapid phosphatizing at heavy bath loading and at temperatures below, and in some cases far below, 80° C. Indeed it has been found possible to keep the concentration of NO₂ constant at an amount of 0.01–0.03% over long periods of time while operating continuously even with the heaviest bath loadings yet without having to add alkali-metal nitrite in the usual continuous or frequent manner.

According to the invention there is provided a process for the production of coatings of zinc phosphate upon surfaces of iron steel, and galvanized iron and steel, as well as zinc and cadmium and their alloys, in which the surfaces are contacted until a coating is formed thereon with an aqueous acidic phosphatizing solution which contains phosphate, zinc and nitrate ions, the initial phosphatizing solution containing zinc phosphate and nitrate ions in a ratio of:

$P₂O₅:Zn:NO₂ = 1 : (1.4 to 2.6) : (2.0 to 4.3)$

and in which the phosphatizing solution is replenished during use whenever necessary to make good the zinc the phosphate ions consumed, replenishment being effected with a replenishment material which contains phosphate, zinc and nitrate ions in a ratio of:

$P₂O₅:Zn:NO₂ = 1 : (0.40 to 0.53) : (0.45 to 0.70)$

and in which, independently of the consumption of zinc and phosphate ions, nitrite is added to the solution only at the beginning of the coating cycle so as to establish a concentration of at least 0.01% NO₂ therein and is thereafter maintained by autocatalytic generation throughout the coating cycle, the temperature of the phosphatizing solution being maintained below 75° C.

Provided that the initial solution is made up within the specified ratio sufficient nitrite is automatically formed in the solution to completely precipitate substantially all of the dissolved iron and to achieve a sufficient acceleration of the phosphatizing process, and consequently the phosphatizing solution will remain substantially nitrite-free for a long time, for example for a matter of months. Preferably more than 70% of the zinc in the initial solution should be in the form of zinc nitrate.

For practical commercial operations the temperature of the phosphatizing solution should of course always be maintained above 45° C, and as will be indicated hereinafter the preferred temperatures are well within the range of 45°–75° C.

To establish the necessary nitrite concentration in the solution it is necessary at the commencement of a cycle of operations with a freshly-prepared initial solution to add nitrite to the solution in such an amount as to establish a concentration therein of at least 0.01% and preferably about 0.014% of NO₂—the nitrite can conveniently be added in the form of a solution of sodium nitrite. No further nitrite need be added thereafter in the course of that working cycle, since nitrite will be autocatalytically generated from the nitrate present in an amount sufficient to maintain a concentration of at least 0.01% NO₂ and often as great as 0.03% NO₂. Indeed, it seems that the bigger the throughput of metal, the greater is the amount of nitrite which is autocatalytically generated. However, when recommencing operations with a previously-used solution, bearing in mind that nitrite breaks down in aqueous acid phosphatizing solutions of this type, it may be necessary before the new working cycle commences to add nitrite again, so as to re-establish a concentration of at least 0.01% NO₂. Normally, sufficient nitrite is still present after an overnight shutdown to make the addition of nitrite unnecessary, and even after a week-end shutdown there is usually some nitrite still present so that only a very small amount of nitrite need be added to bring the concentration of NO₂ up to at least 0.01%.

The process of the invention has the great advantage that it is unnecessary to add sodium nitrate at least several times daily and possibly (depending on the throughput of metal) continuously—on the contrary, it is only necessary to add a small quantity of sodium nitrate once or at the beginning of a working cycle, thus normally only once at the beginning of each week. The control of the process is therefore greatly simplified, and the phosphatizing solution can be used successfully despite a continuous high throughput of metal. Moreover, since little sodium is introduced in the form of nitrate and some need be introduced in the replenishment material, the solution can be kept largely free from sodium ions, which are of course detrimental to coating formation.

A further important advantage of the process of the invention is that coating formation proceeds so rapidly that there is practically no time for ferrous ions dissolved from the iron surface during coating formation to diffuse into the phosphatizing solution, so that sludge formation in the solution is only very slight, and significantly less than in the known phosphatizing processes which involve frequently-repeated or continuous additions of sodium nitrate. Consequently the phosphatizing solutions used in the process of the present invention need be de-sludged only very seldom, for instance when used in an immersion process at normal throughputs perhaps only every 4–6 months. While we do not wish to be limited by theoretical considerations, the absence of heavy sludging can probably be explained by some of the dissolved iron, and perhaps much of it, being incorporated as iron phosphate into the zinc phosphate coating, due to the rapidity of the formation of the coating.

Naturally, the phosphatizing solution must also be replenished whenever necessary, and usually at least several times a day, with phosphate, zinc and nitrate ions in order to replace these as they are consumed in the coating reaction. As already indicated, it is necessary for the success of the process of this invention that the replenishment material should contain phosphate, zinc and nitrate ions in the previously-specified ratios, but in other respects the replenishment is carried out in the usual manner, by adding a concentrate containing the necessary ratios of phosphate, zinc and nitrate ions whenever appropriate. The consumption of phosphate and zinc ions in the coating reaction can be monitored in the conventional manner by determining the total phosphate as measured by the number of millilitres of N/10 NaOH needed to titrate a 10 millilitre sample of the bath to a red end-point using phenolphthalein as indicator; the total phosphate thus determined may then be raised to the desired value by adding a definite quantity (depending on the total volume of the phosphatizing solution in the bath) for each point to be restored. Actually, the total phosphate of the solution is not critical since the process of the invention will produce good phosphate coatings to a large extent independently of the total phosphate, thus both at low and high pointages, but as a general rule one replenishes as to restore the total phosphate to approximately its original value, which preferably will be in the range of 30–40.

Besides total pointage, which is a measure of the total acidity of the solution, there is however another related factor which affects the process, namely the free-acidity of the solution. The ratio of total acidity to free acidity is a significant factor in the extent both the speed of coating formation and the rate at which autocatalytic generation of nitrite takes place. In general, the lower the ratio of total acid to free acid and hence the more free acid there is present in the phosphatizing solution, the faster will coating formation take place and
the more surely will nitrite be autocatalytically generated in sufficient quantities. However, it is not usually practicable to operate the process with a phosphatizing solution having an excess of less than about 5, and indeed the freshly-prepared initial solution will preferably be made up so as to contain only such an amount of phosphate as will yield an acid ratio of from 5 to 8, the optimum acid ratio in the initial phosphatizing solution being usually 7, though this is to some extent dependent on the hardness of the water used for making up the phosphatizing solution.

In the course of the process, however, as the coating reaction proceeds both the total acid and the free acid in the phosphatizing solution tend to diminish. Since the free acid diminishes more quickly than the total acid, the natural tendency is for the acid ratio in the phosphatizing solution to rise. The tendency however is counteracted by the use of the previously specified replenishment material, which is strongly acidic, indeed substantially more so than the hydrolysis equilibrium. The replenishment material preferably has an acid ratio of about 2.8 to 3.7, much lower than that of the initial solution.

According to the ultimate purpose of the zinc phosphate coatings produced by the process of the invention, there is some difference in the optimum acid ratio which should preferably be maintained in the phosphatizing solution, and indeed also in certain other process conditions such as temperature and time of treatment.

Both for the production of corrosion-resistant paint-bonding zinc phosphate coatings and also for the production of zinc phosphate coatings intended, with or without added lubricant, to facilitate subsequent cold forming or other chipless deformation operations by acting as a lubricant coating, it has been found best to reduce the acid ratio, by adding replenishment material, to a value not less than 6. However, whereas in the production of corrosion-resistant zinc phosphate coatings it is advisable to replenish whenever necessary to prevent the acid ratio in the phosphatizing solution from rising above about 9, it is possible in the production of lubricant coatings to allow the acid ratio to rise substantially beyond 9.

In the production of a lubricant coating on particularly reactive metal surfaces, for instance steel wire containing 0.3–0.9% C and 0.4–0.7% Mn, useful coatings can still be obtained even with acid ratios of 16. However, on balance of various considerations, including minimization of sludge formation and greater assurance of adequate autocatalytic generation of nitrite, we prefer that the replenishment should take place even in the production of lubricant coatings before the acid ratio exceeds 10, and recommend that in the production of corrosion-resistant coatings it should take place at or about an acid ratio of 9 though this is not absolutely essential.

As a general recommendation we also prefer that the ratios of zinc and nitrate relative to phosphate in the initial solution should be at the numerically-lower end of the previously stated ranges, thus say

$$\text{P}_2\text{O}_5:\text{Zn:NO}_3 = 1: (1.4 \text{ to } 2.0): (2.0 \text{ to } 3.2)$$

and similarly the ratio of zinc to phosphate in the replenishment material should be at the numerically-lower end of the previously stated range, thus say

$$\text{P}_2\text{O}_5:\text{Zn:NO}_3 = 1: (0.40 \text{ to } 0.47): (0.45 \text{ to } 0.70)$$

Conversely, in the production of corrosion-resistant coatings the ratios of zinc and nitrate to phosphate in both the initial phosphatizing solution and also in the replenishment material can with advantage lie at the upper end of the previously-stated ranges.

As regards the temperatures at which the process is operated, we have found that for the production of corrosion-resistant coatings it is best to avoid the highest temperatures, namely those below 55 °C, and usually most advantageous to employ a temperature in the range of 60–70 °C.

For general guidance it may also be added that the more highly reactive is the metal surface under treatment and/or the heavier is the bath loading, the higher should be the temperature at which the process is operated, in order to ensure adequate autocatalytic generation of nitrite. Even so, it is obviously not impossible so to overload the phosphatizing solution with excessive metal throughputs that the nitrite generated becomes inadequate. This condition however can be recognized either by the green colouration imparted to the phosphatizing solution by soluble ferrous salts or by various methods available today for detecting and measuring ferrous and/or nitrite ion; and removal of the excess bath-loading will then correct the condition. Moreover, the process of the invention is able to handle remarkably heavy bath-loadings, as shown by the following illustration:

A zinc phosphate solution of 39 points, operated in accordance with this invention with an acid ratio of 9 at a bath-loading of 8 m.2 per m.3 of solution at 57°C, gives very satisfactory phosphate coatings and in particular it remains iron-free, i.e. sufficient nitrite is generated autocatalytically. When however at the same temperature the bath-loading is increased to 65 m.2 per m.3 of solution, then the phosphatizing solution after the treatment will be found to contain iron. On increasing the temperature to 65°C, however, the solution is found to remain iron-free even at this higher bath loading, while at a temperature of 70°C, even at a bath-loading of 100 to 110 m.2/m.3 solution, the phosphatizing solution both during and after phosphatizing contained practically no ferrous ions.

The optimum time of treatment also varies somewhat according to the intended purpose of the fine-grained, uniform and dense zinc phosphate coatings produced. For corrosion-resistant coatings a treatment time of from 2 to 5 minutes at 50–60°C will usually be required with the solutions described above to produce a coating having a weight of about 2.5–4.5 g./m.2. For lubricant coatings a treatment time of from 1 to 5 minutes will usually be required with the previously-described solutions to produce a coating having a weight of 3.5–6.0 g./m.2, while at temperatures of 70–75°C the treatment time may be less than 1 minute.

However, if a metallic catalyst, such as nickel, cobalt or copper in the form of soluble salts such as sulphate, nitrate or carbonate, is added to the phosphatizing solution in small amounts such as 0.0025% Ni and/or 0.00135% Cn, the coating weights obtained are 10–20% higher. For the production of heavier coating weights it is therefore desirable to incorporate nickel, copper and/or cobalt in amounts exceeding 0.001%.

Copper and/or nickel and/or cobalt when present in greater amounts of 0.0055%–0.0165% act not only as accelerators, but also seem markedly to promote autocatalytic nitrite-formation and may advantageously be incorporated in these amounts whenever nitrite-formation is inadequate, for instance because the bath-loading is too small or the desired treatment time too short. Copper can be incorporated in the phosphatizing solution for instance by adding 1% to the concentrate as basic copper carbonate.

In order that the invention shall be more clearly understood it will now be described in more detail, but only by way of illustration, with reference to the following examples:

**EXAMPLE I**

A phosphatizing solution with a volume of 500 litres was made up from zinc oxide, nitric acid and phosphoric acid so that it contained 6.3 grams of phosphate (calculated as P2O5 per litre, 12.3 grams of zinc per litre,
and 20.4 grams of nitrate (calculated as NO₃) per litre. Before commencing operations at the beginning of the working week a 24% (by weight) solution of sodium nitrite remained in the phosphatizing solution in an amount corresponding to 0.1% (by volume) per 100 litres, thus establishing a nitrite content of 0.014%. The phosphatizing solution had a total pointage of about 35, and after the addition of the sodium nitrite an acid ratio of 8.

Iron sheet was first degreased with alkali, rinsed, pickled in sulphuric acid and once more rinsed, and was then immersed in this phosphatizing solution at a temperature of 52° C. for a period of 5 minutes, and the coatings formed were very fine-grained, even and dense. After 44 square metres of iron surface had been processed in the 500 litres of solution within the space of two hours (thus, at a bath loading of 44 m.² per m.³ per hour) the nitrite content in the solution was found to have risen to 0.024%, nearly double the initial NO₃ concentration—and moreover, this high nitrite content remained practically constant during the whole working day, despite even heavier loading of the bath.

Replenishment of the solution was carried out whenever its total pointage had fallen by about 2–3 points and before acid ratio had reached 9.0, using a concentrate which contained 383 g./l. P₂O₅, 192 g./l. zinc and 247 g./l. NO₃ (the acid ratio being 3.3, and the ratio P₂O₅:Zn:NO₃ being 1:0.5:0.64).

It is of course to be understood that the term “acid ratio” is used in this example and elsewhere in its conventional sense, namely as the quotient of the total acid pointage divided by the free acid pointage—and that the total acid pointage corresponds to the millilitres of N/10 NaOH which are needed for titrating 10 millilitres of the phosphatizing solution with phenolphthalein as indicator to the red end-point, while the free acid pointage corresponds to the millilitres of N/10 NaOH needed for titrating 10 millilitres of the phosphatizing solution using methylorange as indicator to the red/yellow end-point.

EXAMPLE II

A phosphatizing solution was made up with a content of 7.43 g./l. P₂O₅, 12.93 g./l. Zn and 22.7 g./l. NO₃, having a pointage of 40. A 24% solution of sodium nitrite was added to this phosphatizing solution at the beginning of the working week in an amount of approximately 0.1 vol. percent so as to establish a nitrite concentration of 0.0136%. Steel wires (containing 0.8% C and 0.7% Mn) were phosphated in this solution prior to cold drawing. After a throughput of 213 m.² of wire surface per m.³ of solution, the nitrite concentration had already risen in 2½ hours at 65° C. to 0.0214%, that is by about 57%. This phosphatizing solution was then operated for so long and with so great a bath loading than 400 kg. of a replenishment concentrate containing 370 g./l. P₂O₅ 162 g./l. zinc and 183 g./l. NO₃ (corresponding to a quantitative ratio of P₂O₅:Zn:NO₃=1.0.438:0.498) had to be added per m.² of solution in order to keep the pointage of the solution constant, yet the concentrations of the individual components of the solution remained substantially constant and also the acid ratio was maintained within the limits of 7–10. Moreover, during the whole working week no further sodium nitrite was added to the solution, but nevertheless the concentration of NO₃ in the solution varied only between the values of 0.0160% and 0.0213%.

The excellence of the phosphate coatings produced is shown by the fact that the phosphate coating on the wires remained unbroken even after the wire had been drawn down ten times.

EXAMPLE III

A phosphatizing solution of the same composition as in Example II was prepared, and on the first working day of the week a 24% solution of sodium nitrite was added thereto so as to establish a concentration of 0.0118% NO₃. After a throughput of 51 m.² of wire surface per m.³ of solution in 4 hours at 72° C., the concentration of nitrite in the solution had risen without any further addition of sodium nitrite to 0.0163% NO₃, or about 38%, and it rose further during the rest of the day to 0.0194% NO₃.

Overnight shut-down caused a break in working during which the nitrite concentration dropped to 0.0146% but this was still sufficient to enable the solution to be put into operation again next morning without any addition of sodium nitrite. After a further throughput of 173 m.³/m.² in 3 hours at 38° C., the NO₃ concentration had risen to 0.0245%, corresponding to an increase of 66%.

During the whole working week the nitrite concentration held itself steadily during actual working at about 0.02% without further addition of sodium nitrite, with the result that the pointage of the solution could be held constant at 39–40 points by suitably frequent addition of the concentrate described in Example II. Neither the amounts of the other components of the solution nor the acid ratio altered to any extent. The phosphatized wires thus obtained could moreover be drawn quite satisfactorily.

We claim:

1. A process for the production of coatings of zinc phosphate upon surfaces of iron, steel, zinc (including galvanized iron and steel) and cadmium and their alloys, in which the surfaces are contacted until a coating is formed thereon with an aqueous acidic phosphatizing solution which contains phosphate, zinc, and nitrate ions, and a metallic accelerator selected from the group consisting of copper, nickel and cobalt and mixtures thereof, the initial phosphatizing solution containing phosphate zinc and nitrate ions in a ratio of:

\[ P_2O_5:Zn:NO_3 = 1:(1.4 \text{ to } 2.6):(2.0 \text{ to } 4.3) \]

and in which the phosphatizing solution is replenished during use whenever necessary to make good the zinc and phosphate ions consumed, replenishment being effected with a replenishment material which contains phosphate, zinc and nitrate ions in a ratio of:

\[ P_2O_5:Zn:NO_3 = 1:(0.40 \text{ to } 0.53):(0.45 \text{ to } 0.70) \]

and in which, independently of the consumption of zinc and phosphate ions, nitrite is added to the solution at the beginning of a coating cycle so as to establish a concentration of at least 0.01% NO₃ therein and is thereafter maintained by autocatalytic generation throughout the coating cycle, and in which there is added from 0.0055% to 0.0165% of the metallic accelerator, and maintaining the temperature of the phosphatizing solution below 75° C.

2. A process according to claim 1 wherein steel wires are contacted with the solution to form thereon a coating.

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RALPH S. KENDALL, Primary Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,520,737 Dated July 14, 1970

Inventor(s) Peter Gerassimoff and Paul Dingeldey

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

Column 3, line 30, "the" should read --and--.

Column 4, line 6, "nitrate" should read --nitrite--.

Column 4, line 14, "throughout" should read --throughput--.

Column 4, line 28, "nitrate" should read --nitrite--.

Column 6, line 52, "Cn" should read --Cu--.

November 3, 1970

(SIGNATURE)
Attest:
Edward M. Fletcher, Jr.
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WILLIAM E. SCHUYLER, JR.
Commissioner of Patents