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3,810,792

PROCESS FOR THE APPLICATION OF PHOSPHATE COATINGS ON STEEL, IRON AND ZINC SURFACES

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U.S. Cl. 148—6.15 Z

4 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in the process for the application of phosphate coatings on steel, iron and zinc surfaces comprising contacting steel, iron and zinc surfaces with an acidic solution containing layer-forming cations, phosphate ions, fluoride ions and oxidizing agents for a time sufficient to effect phosphatizing and recovering said phosphatized surfaces. The improvement resides in utilizing from 59 to 100 mol percent of nickel cations as said layer-forming cations in combinations with from 0 to 41 mol percent of other known divalent layer-forming cations. The invention also resides in the acidic phosphatizing solutions.

THE PRIOR ART

Layers of difficultly-soluble metal phosphates have, as is known, for a long time been applied to steel, iron and zinc surfaces for the purpose of corrosion protection and for the improvement of lacquer adhesion. This process is commonly known as phosphate coating or phosphatizing. For this purpose, the metal surfaces are contacted with aqueous acidic solutions of metal phosphates, whose metal cations enter into the coatings. At the beginning of the phosphatizing technique for this purpose, mainly iron or manganese phosphate solutions were used. Newer phosphatizing processes, however, work above all with solutions that contain zinc phosphate as layer-forming component. Also phosphatizing solutions have become known which, besides zinc ions, also contain other layer-forming divalent metal cations, such as calcium, manganese, iron, nickel, cobalt or cadmium cations. With these phosphatizing solutions, the amounts of the layer-forming cations present are generally calculated so that the zinc cations form the substantial portion of the total layer-forming cations.

It has also been known that the named phosphatizing solutions can be modified by a number of additives. Thus, they contain, as a rule, oxidizing agents for the acceleration of the layer formation. In addition, they also may contain copper salts, titanium salts, boric acid, silicic acid and both simple and complex fluorides, in order to attain certain effects.

The best of the actually known processes for the layer-forming phosphatizing of steel, iron and zinc surfaces are, however, in some respects insufficient. Thus, in the continuous treatment of strip material in coil-coating installations, it is in many cases impossible to obtain a closed, dense phosphate layer within the given liquid contact times. Furthermore, the phosphate layers, obtained by the known commercial processes do not exhibit the desired resistance during a subsequent mechanical shaping of the work pieces, for example, by bending or deep-drawing. In these cases, very frequently fissuring or scaling of the phosphate layers or of the lacquer or synthetic resin layers, applied above them, is observed.

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OBJECTS OF THE INVENTION

An object of the present invention is the obtention of acidic phosphate solutions for application of phosphate coatings on iron, steel and zinc surfaces consisting essentially of water containing (1) from 2.0 to 10.0 gm./liter of oxidizing agents, calculated as nitrate ions, (2) from 0.1 to 5.0 gm./liter of complex fluoride ions, (3) from 0.5 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 100 mol percent of nickel cations and (b) 0 to 41 mol percent of divalent metal cations selected from the group consisting of calcium, manganese, iron, cobalt, cadmium and zinc, and (4) an amount of phosphate ions at least sufficient to form dihydrogen phosphates with said divalent layer-forming metal cations, said acidic phosphate solutions having a total acid of from 5 to 30 points, a free acid of from 0.5 to 6 points and a ratio of total acid to free acid in points of from 5:1 to 10:1.

A further object of the present invention is the development of, in the process for the application of phosphate coatings on steel, iron and zinc surfaces consisting essentially of contacting steel, iron and zinc surfaces with an acidic aqueous solution containing di-valent layer-forming metal cations, phosphate ions, fluoride ions and oxidizing agents for a time and at a temperature sufficient to effect formation of a phosphate coating on said surfaces, and recovering said phosphate coated steel, iron and zinc surfaces, the improvement which consists in utilizing (a) from 59 to 100 mol percent of nickel cations and (b) from 0 to 41 mol percent of divalent layer-forming metal cations other than nickel, as said divalent layer-forming cations.

A yet further object of the invention is the development of a continuous process for obtaining continuous phosphate layers on iron, steel and zinc surfaces having less than 1.0 gm./m.² of layer weight.

These and other objects of the invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The present invention relates to a process for the application of phosphate layers on steel, iron and zinc surfaces with the aid of solutions that contain film-forming cations, phosphate ions, fluoride ions and oxidizing agents. Hereafter, the term "zinc surfaces" shall include both surfaces of objects from zinc and zinc alloys and galvanized iron and steel surfaces.

It has now been found, that the above-named defects of the prior art can be overcome and the object of the invention can be achieved, if the below-described process for the application of phosphate layers on steel, iron or zinc surfaces is employed. The novel process is carried out with acidic solutions, that contain layer-forming cations, phosphate ions, fluoride ions and oxidizing agents. It is characterized in that the metal surfaces are treated with solutions, that contain as layer-forming cations substantially nickel ions.

In the solutions for carrying out the invention process, in the simplest case only nickel ions are present as layer-forming cations. However, it has been found advantageous to employ solutions that contain, besides nickel ions, also a minor amount of layer-forming cations of another divalent metal. As such other divalent cations, calcium, manganese, iron, cobalt, cadmium, and preferably zinc ions can be utilized. The amounts of the layer-forming cations are thereby calculated so that the molar ratio of nickel ions to the other divalent metal cations is in the range of 1:0.001 to 1:0.7. The overall molar ratio of nickel ions to the other divalent layer-forming metal cations in the process of the invention is, therefore, from 1:0 to 1:0.7. The total amount of layer-forming cations employed in

the process of the invention consists, therefore, of (a) from 59 to 100 mol percent of nickel cations and (b) from 0 to 41 mol percent of divalent layer-forming metal cations, other than nickel.

The invention, therefore, involved, in the process for the application of phosphate coatings on steel, iron and zinc surfaces consisting essentially of contacting steel, iron and zinc surfaces with an acidic aqueous solution containing divalent layer-forming metal cations, phosphate ions, fluoride ions and oxidizing agents for a time and at a temperature sufficient to effect formation of a phosphate coating on said surfaces, and recovering said phosphate coated steel, iron and zinc surfaces, the improvement which consists in utilizing (a) from 59 to 100 mol percent of nickel cations and (b) from 0 to 41 mol percent of divalent layer-forming metal cations other than nickel, as said divalent layer-forming metal cations.

The divalent layer-forming cations are employed in the forms such as oxides, carbonates, sulfates, phosphates, nitrates or fluorides introduced into the solutions or charge concentrates.

The applied phosphatizing solutions contain fluorides ions, as a rule in the form of complex fluorides, particularly as fluoborate, fluotitanate and fluosilicate. The complex fluorides can be introduced into the solutions as alkali metal borofluorides, alkali metal fluotitanates and alkali metal fluosilicates or in the form of the corresponding acid complex fluorides. They can, however, also be prepared in situ, for example by addition of boric acid and a corresponding amount of hydrofluoric acid. A slight excess of non-complex bound fluoride is not damaging.

For the acceleration of the layer formation, in the process of the invention, the oxidizing agents, customary in the phosphatizing technique, are utilized. As accelerators, particularly nitrates, chlorates and mixtures of nitrates and chlorates are used. In addition, sodium m-nitrobenzenesulfonate or the combinations nitrite/nitrate or nitrite/chlorate are possible.

Solutions have been found as particularly suitable for the process, that contain 2.0 to 10.0 gm./l. of oxidizing agents, calculated as the nitrate ion, 0.1 to 5.0 gm./l. of complex fluoride ions, 0.5 to 15.0 gm./l. of nickel ions or nickel ions and ions of another divalent metal, preferably of zinc, in a molar ratio in the range of 1:0.001 to 1:0.7 and an amount of PO_4 that is at least sufficient to form dihydrogen phosphate with the divalent metal cations present.

In particular, bath solutions are employed consisting of acidic phosphate solutions for application of phosphate coatings on iron, steel and zinc surfaces consisting essentially of water containing (1) from 3.0 to 10.0 gm./liter of oxidizing agents, calculated as nitrate ions, (2) from 0.1 to 5.0 gm./liter of complex fluoride ions, (3) from 0.1 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 100 mol percent of nickel cations and (b) 0 to 41 mol percent of divalent metal cations selected from the group consisting of calcium, manganese, iron, cobalt, cadmium and zinc, and (4) an amount of phosphate ions at least sufficient to form dihydrogen phosphates with said divalent layer-forming metal cations, said acidic phosphate solutions having a total acid of from 5 to 30 points, a free acid of from 0.5 to 6 points and a ratio of total acid to free acid in points of from 5:1 to 1:1.

The phosphatizing solutions are appropriately prepared by diluting of aqueous concentrates in which the components are already contained in the respective proportions.

The concentration of the active ingredients decreases continuously in the operating phosphatizing baths by layer formation and by bath solution remaining on the metal surfaces. The phosphatizing solutions have, therefore, to be periodically or continuously supplemented. In the invention process, for this, concentrates are used in which the ratio of total acid to free acid in points lies in the range of from 2.5:1 to 6.0:1. Total acid is the amount of milliliters (points of $n/10$ NaOH which is consumed

in the titration of 10 ml. of concentrate to the end point of phenolphthalein. Free acid is defined as the amount of milliliters (points) of $n/10$ NaOH that is required for the titration of 10 ml. of the bath solution against methyl orange.

The process of the invention, therefore, also involves a continuous process for the application of phosphate coatings on steel, iron and zinc surfaces consisting essentially of continuously contacting steel, iron and zinc surfaces with acidic phosphate solutions for application of phosphate coatings on iron, steel and zinc surfaces consisting essentially of water containing (1) from 2.0 to 10.0 gm./liter of oxidizing agents, calculated as nitrate ions, (2) from 0.1 to 5.0 gm./liter of complex fluoride ions, (3) from 0.5 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 100 mol percent of nickel cations and (b) 0 to 41 mol percent of divalent metal cations selected from the group consisting of calcium, manganese, iron, cobalt, cadmium and zinc, and (4) an amount of phosphate ions at least sufficient to form dihydrogen phosphates with said divalent layer-forming metal cations, said acidic phosphate solutions having a total acid of from 5 to 30 points, a free acid of from 0.5 to 6 points and a ratio of total acid to free acid in points of from 5:1 to 10:1, for a time and at a temperature sufficient to effect formation of a phosphate coating on said surfaces, continuously recovering said phosphate coated steel, iron and zinc surfaces, and replenishing said acidic phosphate solutions as required with a concentrate having an ingredient concentration as required to maintain said acidic phosphate solutions as defined, said concentrate having a ratio of total acid to free acid in point of from 2.5:1 to 6.0:1.

The phosphatizing solutions can be applied to the metal surfaces in the dipping, flow coat or spraying processes. With steel and iron surfaces, treating temperatures between 55° C. and 75° C. have been found advantageous. The favorable temperature range for the treatment of the zinc surfaces is between 45° C. and 75° C. For the named temperature ranges, the duration of the treatment amounts to between 2 and 120 seconds, depending upon the desired weight of the coat. If the process is applied in coil-coating installations, the exposure (contact) times lie preferably in the range of from 5 to 15 seconds.

Before the phosphatizing process, the surfaces to be treated are normally alkaline-cleaned and degreased in a conventional way. In certain cases, this precleaning is not required, as for example, when a galvanized material is immediately phosphatized following the galvanizing.

In many cases, it is advantageous to passivate the layers formed with dilute chromic acid and/or phosphoric acid. The concentration of the chromic acid and/or the phosphoric acid utilized is generally between 0.01 and 0.5 gm./l. In a preferred application of the invention, the protective layers are after-treated with dilute chromic acid that contains chromium (III)-ions. Generally here the application concentrations of the hexavalent chromium are between 0.2 and 2 gm./l., calculated as CrO_3 and that of the trivalent chromium are between 0.05 and 1.0 gm./l. calculated as Cr_2O_3 . Between the phosphatizing and the after-treatment step appropriately a rinsing with water can be applied. This rinsing is, however, not absolutely required and above all can be omitted if squeeze rolls are utilized. Subsequently to the after-passivating the phosphate layers are conventionally dried.

With the aid of the novel process, completely continuous, homogenous phosphate layers of yellowish to grayish-black coloring can be obtained on steel, iron and zinc surfaces. These layers adhere very firmly to the metal surfaces, so that the work pieces so phosphatized, and optionally provided with a lacquer or synthetic resin coating, may subsequently be mechanically shaped without cracking and scaling of the layers. While it is not possible with the known processes for layer-forming phosphatizing to obtain on zinc surfaces continuous phosphate layers of less than 1.0 gm./m.² layer weight, by the process of the

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invention, by an appropriate selection of the parameters, it is possible to obtain completely unobjectionable coatings with layer weights between 0.2 and 0.5 gm./m.². Furthermore, in the process of the invention the layers are formed with a great reaction speed, so that the short treatment times, required for coil coating installations, can be realized.

The following examples are illustrative of the process of the invention without being deemed limitative in any matter.

EXAMPLE 1

A phosphatizing bath solution of the following composition was prepared:

6.90 gm./l. $\text{Ni}(\text{H}_2\text{PO}_4)_2$
0.14 gm./l. H_3PO_4
0.38 gm./l. HNO_3
1.12 gm./l. NH_4NO_3
2.16 gm./l. NaClO_3
0.59 gm./l. HBF_4

At a total acid concentration of 9.7 points, the concentration of free acid was 1.3 points.

With this solution steel plates were treated in the flow coat process at the following temperatures and exposing times:

55° C.: 30–120 seconds
60° C.: 30–60 seconds
70° C.: 20–30 seconds

Subsequently, the plates were rinsed with tap water, after-passivated with a solution that contained 0.2 gm./l. of CrO_3 , and finally dried in a stream of warm air.

After this treatment, the steel surfaces exhibited hard, dark phosphate layers.

In addition, hot-galvanized steel plates were treated by the flooding process with above-described solution, at the following temperatures and treating times:

50° C.: 15–60 seconds
60° C.: 8–30 seconds
70° C.: 5–15 seconds

After an intermediary rinsing with water, the plates were after-passivated, as described above, and subsequently dried. On the galvanized surfaces ocher-colored to greyish-black phosphate layers were obtained.

All coatings, prepared with this solution, were completely continuous and regularly formed. At short treatment times and low temperatures, very thin layers were obtained. Longer exposing times and/or higher temperatures resulted in thicker layers and thus higher median weights. The coatings were very well suited as an adhesion base for subsequently applied lacquer and synthetic resin layers. The coated plates could be bent or deep-drawn without damage to the coatings.

EXAMPLE 2

A phosphatizing solution of the following composition was prepared:

2.70 gm./l. of $\text{Zn}(\text{H}_2\text{PO}_4)_2$
5.65 gm./l. of $\text{Ni}(\text{H}_2\text{PO}_4)_2$
0.45 gm./l. of H_3PO_4
0.47 gm./l. of HNO_3
4.10 gm./l. of NH_4NO_3
0.73 gm./l. of HBF_4

The free acid concentration was 2.0 points and the total acid concentration was 12.3 points.

Standard plates of cold-rolled steel of the grade St 14.05 were treated with this solution in the dipping process at the following temperatures and dipping times:

0° C.: 10–60 seconds
60° C.: 10–30 seconds
70° C.: 10–20 seconds

Subsequently to the phosphatizing the plates were rinsed with cold water, after-treated with a solution that

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contained 0.6 gm./l. of chromium (VI) ions and 0.2 gm./l. of chromium (III) ions for 15 seconds at 65° C. and dried.

In all cases, unobjectionable, thin phosphate layers were obtained.

In an analogous manner standard plates of hot-galvanized steel were treated in the dipping process at the following temperatures and exposure times:

40° C.: 20–60 seconds
50° C.: 10–30 seconds
60° C.: 5–10 seconds

In all tests, a completely homogenized formation of the phosphate layer was observed.

The phosphate layers produced on the surfaces of steel and hot-galvanized material are an excellent adhesion base for lacquer and synthetic resin coats. The layers are not damaged in subsequent mechanical shaping. In corrosion tests, they were, as shown by condensed water and salt spray tests, mostly superior to the known zinc phosphate layers, or at least equivalent.

In the above specified solution, the borofluoric acid may be replaced by equivalent amounts of fluosilicic acid or potassium fluotitanate, without any essential changes in the quality of the coatings.

EXAMPLE 3

An aqueous concentrate was prepared by mixing of the following ingredients:

1.7 parts by weight of ZnO
5.3 parts by weight of NiCO_3
19.6 parts by weight of a 75% H_3PO_4 solution
3.0 parts by weight of a 49% HBF_4 solution
7.3 parts by weight of NaClO_3
62.8 parts by weight of water

From 4 parts by weight of this concentrate and 96 parts by weight of water, a phosphatizing bath solution of the following composition was obtained:

2.16 gm./l. of $\text{Zn}(\text{H}_2\text{PO}_4)_2$
4.50 gm./l. of $\text{Ni}(\text{H}_2\text{PO}_4)_2$
0.74 gm./l. of H_3PO_4
0.59 gm./l. HBF_4
2.90 gm./l. of NaClO_3

The free acid concentration of this solution was 1.6 points and the total acid concentration was 10.5 points.

With this solution standard plates of cold-rolled steel of the grade St 14.05 were treated in the flow coat process at the following temperatures and exposure times:

50° C.: 10–30 seconds
55° C.: 10–20 seconds
60° C.: 10–15 seconds
70° C.: 5–20 seconds

Subsequently, the plates were rinsed with completely demineralized water and dried. In all cases, thin, completely homogeneous and continuous phosphate layers were obtained. The average layer weight of the coating, depending upon the exposure time and the treating temperature, was in the range from 0.3 to 0.8 gm./m.².

In addition, hot-galvanized steel plates were treated with the same solution in the flooding process at the following temperatures and exposure times:

45° C.: 10–20 seconds
50° C.: 4–15 seconds
55° C.: 2–10 seconds
60° C.: 5–8 seconds

At lower temperatures and short treating times, yellowish to ocher-colored phosphate layers were attained. With increasing temperatures and/or longer exposing times, the color of the layers changed to grey to greyish black. Correspondingly, the average layer weight of the coating rose from 0.2 to 0.6 gm./m.². In all cases, the layers were formed unobjectionably.

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EXAMPLE 4

A phosphatizing solution of the following composition was prepared:

4.56 gm./l. of $\text{Ni}(\text{H}_2\text{PO}_4)_2$
 2.11 gm./l. of $\text{Zn}(\text{H}_2\text{PO}_4)_2$
 0.33 gm./l. of H_3PO_4
 1.24 gm./l. of HNO_3
 2.12 gm./l. of NaClO_3
 0.59 g.m/l. of HBF_4

The total acid concentration was 10.1 points. By the addition of ammonium hydrogencarbonate the ratio of free acid to total acid was adjusted to the value 8.5.

With this solution steel plates were treated for 5 seconds at 60° C. and standard plates of hot-galvanized steel were treated for 5 seconds at 50° C., both by a spraying process. After an intermediary rinsing with tap water, the layers produced were treated with an after-passivating solution, containing 0.1 gm./l. of phosphoric acid and 0.1 gm./l. of chromic acid, for 5 seconds at 60° C. or 50° C. respectively and subsequently dried in a stream of hot air.

The steel surfaces possess after this treatment dark-grey to greyish-black phosphate coats with an average layer weight of coating of 0.3 to 0.4 gm./m.².

On the galvanized steel surfaces, ocher-colored phosphate layer were obtained, whose average layer weight of coating was 0.2 to 0.3 gm./m.². In all cases, the layers were dense and completely homogeneously formed.

Comparable results were attained if, in the above described solutions, fluoboric acid was replaced by the equivalent amounts of fluosilicic acid or potassium fluotitanate.

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art or disclosed herein, may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. In the process for the application of phosphate coatings on steel, iron and zinc surfaces consisting essentially of contacting steel, iron and zinc surfaces with an acidic aqueous solution containing divalent layer-forming metal cations, phosphate ions, fluoride ions and oxidizing agents for a time and at a temperature sufficient to effect formation of a phosphate coating on said surfaces, and recovering said phosphate coated steel, iron and zinc surfaces, the improvement which consists in utilizing from 0.5 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 99.9 mol percent of nickel cations and (b) from 0.1 to 41 mol percent of zinc cations.

2. The process of claim 1 wherein said fluoride ions are complex fluoride ions.

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3. A continuous process for the application of phosphate coatings on steel, iron and zinc surfaces consisting essentially of continuously contacting steel, iron and zinc surfaces with acidic phosphate solutions for application of phosphate coatings on iron, steel and zinc surfaces consisting essentially of water containing (1) from 2.0 to 10.0 gm./liter of oxidizing agents, calculated as nitrate ions, (2) from 0.1 to 5.0 gm./liter of complex fluoride ions, (3) from 0.5 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 99.9 mol percent of nickel cations and (b) 0.1 to 41 mol percent of zinc cations, and (4) an amount of phosphate ions at least sufficient to form dihydrogen phosphates with said divalent layer-forming metal cations, said acidic phosphate solutions having a total acid of from 5 to 30 points, a free acid of from 0.5 to 6 points and a ratio of total acid to free acid in points of from 5:1 to 10:1, for a time and at a temperature sufficient to effect formation of a phosphate coating on said surfaces, continuously recovering said phosphate coated steel, iron and zinc surfaces, and replenishing said acidic phosphate solutions as required with a concentrate having an ingredient concentration as required to maintain said acidic phosphate solutions as defined, said concentrate having a ratio of total acid to free acid in points of from 2.5:1 to 6.0:1.

4. Acidic phosphate solutions for application of phosphate coatings on iron, steel and zinc surfaces consisting essentially of water containing (1) from 2.0 to 10.0 gm./liter of oxidizing agents, calculated as nitrate ions, (2) from 0.1 to 5.0 gm./liter of complex fluoride ions, (3) from 0.5 to 15.0 gm./liter of divalent layer-forming metal cations consisting of (a) from 59 to 99.9 mol percent of nickel cations and (b) 0.1 to 41 mol percent of zinc cations, and (4) an amount of phosphate ions at least sufficient to form dihydrogen phosphate with said divalent layer-forming metal cations, said acidic phosphate solutions having a total acid of from 5 to 30 points, a free acid of from 0.5 to 6 points and a ratio of total acid to free acid in points of from 5:1 to 10:1.

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50 RALPH S. KENDALL, Primary Examiner

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148—6.15 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,810,792

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Inventor(s) Christian Ries and Margot Prymka

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

Patent

Appln.

<u>Col.</u>	<u>Line</u>	<u>Page</u>	<u>Line</u>
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In the heading
in column 1
the second in-
ventor's name
should be
spelled as
follows:

--Margot Prymka--

In the heading
in column 1
the correct
spelling of
the name of
the Assignee is:

--Gerhard Collardin GmbH--

3	75	8	6	"(points" should read --(points)--
5	52	12	12	"beat" should read --bent--
5	70	13	1	"0°" should read -- 50° --

Signed and sealed this 11th day of March 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks