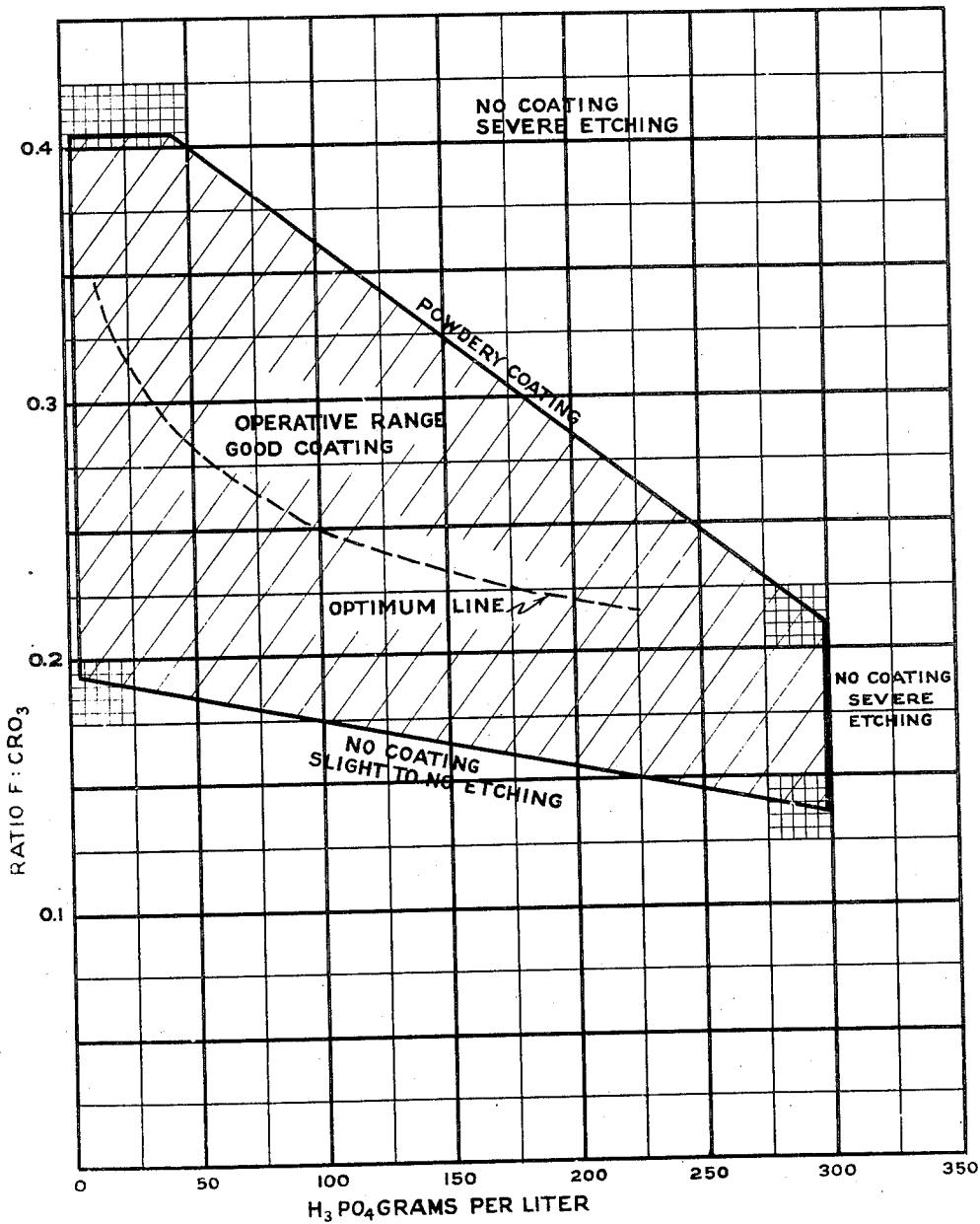


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METHOD OF COATING FERRIFEROUS
METALS AND ZINCIFEROUS METALS
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OPERATING RANGE CHART USING AN ALKALI FLUORIDE,
CHROMIC ACID, AND PHOSPHORIC ACID



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METHOD OF COATING FERRIFEROUS
METALS AND ZINCIFEROUS METALS

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This invention relates to the art of coating ferriferous surfaces and zinciferous surfaces such, for example, as iron, zinc, steel, galvanized metals and galvanneal metals, the latter being the trade name for a galvanized surface which has been annealed. It is particularly directed to a simple process for producing a coating which renders the surface highly corrosion resistant and an excellent base for paint or other similar organic finish.

The principal objects of the invention are to increase, under normal service conditions, the durability of ferriferous and zinciferous metal surfaces; to improve their resistance to humid or salt-laden atmospheres; to improve the degree of durability of the protection afforded by paints, lacquers, etc.; to provide a coating which, essentially, is a phosphate coating and one which can be produced with great rapidity yet without the necessity of using supersaturated solutions or special accelerating agents in the manner which has heretofore been customary in the art; to provide a process which results in very little, if any, sludge; and to obtain the foregoing objectives by means which are more simple and more economical than any which have been employed hitherto.

The foregoing, together with such other objects and advantages as may appear hereinafter or are incident to our invention, are attained in accordance with the following disclosure which describes preferred materials and conditions useful in carrying out our invention.

The present invention is based upon the discovery that the treatment of ferriferous and zinciferous surfaces with aqueous acid solutions containing phosphoric acid, chromic acid and a water soluble compound of fluorine in a certain well-defined region as to the proportions of the ingredients, leads to the formation of a strongly adherent coating which has outstanding merit in inhibiting corrosion and improving paint adhesion and durability. On ferriferous surfaces the coating is smooth and apparently amorphous and of a dull, drab, grayish to shiny or colorless appearance, while on zinciferous surfaces the coating apparently is microcrystalline in structure and has a dull, drab color usually grayish in hue. On both metals, however, the coatings are extremely adherent because the solutions of the invention appear to react with the surface of the metal so that the coating is substantially integrated with the surface.

Generally speaking, our novel coating process makes use of an aqueous acid solution containing phosphate ions, fluoride ions, and dichromate

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ions. The form in which the ions are introduced seems to make little or no difference as long as these remain in the solution in the correct proportions and the solution has the proper acidity. For instance, the phosphate ion may be introduced as phosphoric acid or as a salt of phosphoric acid such as monosodium, monopotassium or mono-ammonium phosphate; the fluoride ion may be introduced as a solution of hydrofluoric acid, as sodium fluoride, or as potassium acid fluoride; the dichromate ion may be introduced as chromic acid (CrO_3), as potassium, or as sodium chromate or dichromate. Naturally the amount of acid which is to be added will depend upon the form in which the essential ions are added to the solution, as will be further explained below.

The kind and quantity of cations which may be present are not in themselves important except insofar as their salts act as buffers to regulate the effective acidity of the solution, or as they may cause the loss of active anions by precipitation of salts whose solubility products may be exceeded. Among the cations which may be present in reasonable quantity without doing harm are those of aluminum, trivalent chromium, zinc, copper, manganese, iron, nickel, cobalt, calcium, barium, strontium, tin and others. Indeed, the presence of limited quantities of cations which are electro-positive to and above hydrogen in the electromotive series has a definitely beneficial effect in increasing corrosion resistance and also in modifying the speed of the coating operation. However, excessive amounts, say over approximately 10 grams per liter of any of these cations may tend to cause a loss of fluoride ion by precipitation, but do no other noticeable harm. Fluoride so lost may be replaced and the solution thus restored to its optimum condition.

Foreign anions may also be present in moderate quantities without causing any difficulty. For example, relatively large amounts of sulphate, nitrate, acetate and chloride ion are tolerated without difficulty. Reducing agents are harmful because they cause a loss of dichromate ion by reduction of hexavalent to trivalent chromium.

The solutions used in performing our improved coating process are characterized by a content of acid, fluoride ion, phosphate ion, and dichromate ion which are within a certain well-defined area. Generally stated, the region of concentrations within which our solutions must be maintained for satisfactory coating is defined as follows:

1. The phosphate ion content must be at least 2 grams per liter, and, preferably, at least 6 grams

per liter, calculated as PO_4 . At concentrations below 6.0 grams per liter the operative concentrations of dichromate ion and fluoride ion become extremely critical; below 2.0 grams per liter it is hardly possible to maintain the dichromate and fluoride concentrations with sufficient accuracy to operate the process even upon a small area of metal per unit volume of bath. At 6.0 grams per liter of PO_4 the range of permissible fluoride and dichromate is large enough to permit practical operation on a succession of pieces. However, even at this concentration rather careful control and frequent restoration of phosphate, fluoride, acid and chromate are necessary to maintain the solution in optimum working condition. A good working concentration of PO_4 content is between 20 and 100 grams per liter. A practical maximum is about 285 grams per liter.

2. The ratio of fluoride ion to dichromate ion, by weight (calculated as chromic acid, CrO_3) must be between 0.135 and 0.405, and, preferably, between 0.18 and 0.36.

Too high a ratio of fluoride ion to dichromate leads to the formation of loose coatings or the absence of coatings and the production of a surface which is merely etched, in contrast with the development of tight, adherent, continuous coatings resistant to abrasion and bending, which are formed under optimum conditions.

A ratio of fluoride ion to dichromate ion which is somewhat too low leads to the development of very thin coatings; at even lower ratios no visible coating action takes place, and the metal remains smooth and bright.

3. The total acidity of the solution must not exceed that corresponding to 3.0 normal acid. For the purposes of this calculation all polybasic acids whose second ionization constants are less than 10^{-4} may be considered to be monobasic. For such acids, the second and subsequent ionizable hydrogen atoms make less than a 1.0% contribution to the hydrogen ion content of their aqueous solutions at $\text{pH}=2.0$ or below. The solutions with which we are dealing have pH 's near or below 2.0. Examples of such acid are phosphoric and arsenic acids.

Somewhat too high an acidity results in a powdery, non-adherent coating; still higher acidity results in a strong etch and no attached coating.

It must be explained that the absolute quantities of acid and of anions which may be present under operative conditions are not independent. The actual hydrogen ion concentration of the solution is a function of the dissociation constants of the acids corresponding to the anions present. In the absence of anions of acids weaker than phosphoric acid, hydrofluoric acid, or chromic acid, the hydrogen ion content of the solution falls with increase in the quantity of phosphate, fluoride, and dichromate. It has been found necessary to have in the solution a greater amount of acid the greater the quantities of these ions present.

It is desirable to express the acidity of the operative solutions in terms of pH . Unfortunately no accurate means of measuring the pH of the solutions has been found. The use of indicators is unreliable because the indicators are oxidized by the dichromate ion present. The electrical pH meter, using the glass electrode is unreliable because of the effect of the fluoride ion upon the glass. The hydrogen and quinhydrone electrodes are likewise inapplicable because of the oxidizing effect of the dichromate.

The glass electrode, however, seems to give readings which, while they often exhibit a curious excursion with time from a low value to a value as much as a pH unit higher, and then back to a value even lower than at first, seem to have some significance, even though they are not unequivocally interpretable. Since a recheck in a standard buffer solution of the glass electrode, after a measurement of one of our coating solutions, shows very little change, it may be assumed that the electrode is not permanently damaged by use for the measurement of the coating solutions.

With these limitations in mind, the final, nearly steady reading of pH , by means of a commercial glass electrode pH meter, in our improved solutions in correct operating condition, falls in the range 1.6 to 2.2 and for optimum coating conditions, in the range 1.7 to 1.9.

To prepare a solution for operating our improved coating process there may be added to water:

1. Sufficient phosphate ion, in the form of phosphoric acid or any phosphate soluble at a pH of about 2, to give a phosphate content (as PO_4) of at least 2 grams per liter, and better, 6.0 grams per liter.

2. Materials containing fluoride and hexavalent chromium in a quantity sufficient to give a ratio of dissolved fluorine to dissolved hexavalent chromium (calculated as $\text{F}:\text{CrO}_3$) of between 0.135 and 0.405, or, preferably, between 0.18 and 0.36. The optimum generally is near 0.27.

3. An acid, preferably one at least as strong as HF , to give an apparent pH as measured by a commercial glass-electrode pH meter of 1.6 to 2.2, or, preferably, from 1.7 to 1.9 as measured by the lowest value indicated within the first 10 minutes of immersion of the glass electrode in the solution.

This step is, of course, subject to the limitations stated above. In any case, provided the phosphate, dichromate, and fluoride are present in the proper quantities, the exact quantity of acid to be used may be checked by the appearance of the coating produced during actual processing of a series of pieces. As stated above, too low an acidity leads to no coating or a very thin coat. Too high an acidity leads to loose powdery coatings, still higher acidity to a strong etch, sometimes preceded by the formation of visible coatings which wash off on removal of the treated part from the bath or on rinsing it with water.

In carrying out our improved process the surfaces to be coated should be clean. The cleaning, which forms no part of the present invention, may be carried out by conventional methods. For example, grease and dirt may be removed by a mild silicate alkali spray or by the use of an emulsion of a grease solvent. Heavy oxide films may be removed by acid or caustic soda treatments. The cleaned work, which may be wet or dry, is treated with a solution of proper composition, of which one example is the following:

Formula 1

70	Phosphoric acid, 75% -----	grams--	64
	Sodium fluoride -----	do----	5
	Chromic acid (CrO_3) -----	do----	10
	Water, to make -----	liter--	1

The treatment may be performed by immersing the surfaces to be coated in the solution, by

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flowing or spraying the solution upon the work, or by other convenient techniques in which the solution is allowed to act upon the work. If the solution is merely applied to the work momentarily after which the adhering film of solution is allowed to act for some time, it is desirable to use a solution considerably more concentrated than that of Formula 1.

The action of the solution may be accelerated by heat. The solution may be kept at any temperature from ordinary room temperature to 180° F. or more. Similar coatings appear to be formed independent of temperature but the time for complete coating formation may be reduced from about 5 to 10 minutes to 1 to 2 minutes, or even less by such a rise in temperature.

A number of alternative bath formulas are given below by way of illustration, illustrating a few of the many variations in composition which the compositions may take within their operating range.

Formula 2

H ₃ PO ₄	grams	12
NaF	do	3.1
CrO ₃	do	3.6
Water, to make	liter	1

Formula 3

H ₃ PO ₄	grams	24
NaF	do	5.0
CrO ₃	do	6.8
Water, to make	liter	1

Formula 4

NaH ₂ PO ₄ ·H ₂ O	grams	31.8
NaF	do	5.0
K ₂ Cr ₂ O ₇	do	10.6
HCl	do	4.8
Water, to make	liter	1

Formula 5

NaH ₂ PO ₄ ·H ₂ O	grams	66.5
NaHF ₂	do	4.2
K ₂ Cr ₂ O ₇	do	14.7
H ₂ SO ₄	do	4.8
Water, to make	liter	1

Formula 6

NaH ₂ PO ₄ ·H ₂ O	grams	31.8
AlF ₃	do	5.0
K ₂ Cr ₂ O ₇	do	10.6
HCl	do	4.6
Water, to make	liter	1

Of these examples of coating solutions Formulas 1, 3 and 4 produced normal weight coatings, and Formulas 5 and 6 produced slightly lighter coatings than normal.

Maintenance of the solutions in operating condition during the processing of a succession of surfaces requires merely that the proportion of dissolved ions and acidity be kept within the prescribed limits by suitable additions of chemicals. It is to be noted that the coating operation consumes chemicals as follows:

1. Acid is consumed by attack on the metal, the reaction being quite calm with little or no gassing.

2. Phosphate and fluoride are included in the coating, as evidenced by its analysis.

3. Dichromate is consumed by reduction to trivalent chromium, some of which is included in the coating, some of which remains dissolved in the solution.

4. The accumulation of dissolved iron or zinc in the solution leads, ultimately, to a loss of fluoride as a precipitate of iron or of zinc fluoride.

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5. Some trivalent chromium may be precipitated when this accumulates to a sufficient degree as the fluoride and/or phosphate.

These losses, as well as gross loss of solution due to "drag-out" on the surface of the work, must be replaced to maintain the bath within its operating limits. The precipitates referred to are of relatively minor consequence because their quantity is exceptionally small and, apparently, they are without effect on the process except as they are mechanically objectionable if allowed to accumulate indefinitely. In any case, they may be removed without difficulty by simple decantation or filtration.

After the treatment with the solution, as described, the coated surfaces can either be rinsed with water and then dried, or be dried first followed by a water rinse and a second drying. In the second instance the adhering treating solution dries upon the coated surface and when it is not desired to paint the surface it may be left in an unrinsed condition after it has been dried. However, if paint or other organic finish is to be applied to the coated and dried surface, it should then be thoroughly rinsed with pure water to remove all soluble salts because such salts are likely to cause blistering of the paint or other organic film, especially if the surface is to be subjected or exposed to humid conditions.

We have found that the corrosion resistance imparted to the surface is distinctly improved by permitting the adhering treating solution to dry upon the coated surface before any rinsing takes place and that such dried and unrinsed surfaces are satisfactory for many purposes where a subsequent organic finish is not desired but, as stated, where paint is to be applied rinsing is necessary to remove any residue of soluble salts which may be present.

The drying of the coated surfaces with their adhering solution may be accomplished at ordinary room temperature or at elevated temperatures where expedition of the drying process is desirable. In the latter event the time and temperature of exposure to the drying oven need be sufficient to remove physical moisture only. Longer heating, especially at temperatures above the boiling point of water, will drive off chemically bound water.

Where paint or other organic finish is to be applied to the coated surface it may be unnecessary in many instances to go to the trouble of an initial drying of the adhering residues of treating solution, in which event the treated surfaces may be immediately rinsed with pure water to remove the soluble salts and then dried. Such treatment yields excellent results although, as indicated above, the corrosion resistance of the coating is not quite equal to that of coatings produced by permitting the adhering treating solution to dry before any rinsing takes place.

If any small amount of soluble salts should be left on the finally dried surface they may be rendered much less harmful if the surface is treated, after coating and drying, with a dilute solution containing free chromic acid. Thus, if there is any possibility that the water used for rinsing is too high in dissolved salts for absolute safety, it has been found desirable finally to rinse the coated and dried surfaces with a dilute chromic acid solution containing from ½ to 8 ounces of chromic acid per 100 gallons of water, after which the surfaces are again dried. This treatment cannot be harmful and may, therefore, be applied as a matter of routine whether or not the

water supply is known to be too high in soluble salts.

We should like to note that, if desired, rinsing of the dried residues of treating solution may in effect be combined with the final chromic acid rinse although to prevent undue contamination of the chromic acid solution we prefer to rinse first with plain water and then with the dilute chromic acid solution.

On ferrous surfaces the coatings produced by our improved process are apparently amorphous in character and are integrally bound to the surface of the treated metal. Analysis shows that they contain iron, fluorine, phosphorus, chromium, oxygen and hydrogen as their principal constituents. On zinciferous surfaces the coating apparently is microcrystalline in structure and has a dull, drab color usually grayish in hue. The principal constituents of the coating on zinciferous metals are the same as on ferrous metals except, of course, that zinc takes the place of iron. The coatings on both metals are substantially integrated with the metal surface and extremely adherent. On heating they lose up to 40% of their weight. Physically such heating seems to produce no obvious change; chemically, however, the coatings tend to become somewhat more corrosion resistant after dehydration by heating.

Although, as previously stated, the coating solutions can be prepared from a variety of starting substances, possibly the simplest, cheapest, and most easily available combination of chemicals from which to prepare them is an alkali fluoride, phosphoric acid and chromic acid (CrO_3).

The limits of composition within which the coating process is operative have been indicated. A very large number of charts and diagrams can be drawn to indicate the operable regions for our solutions and process depending on the starting materials. However, for illustrative purposes, and as a guide to the operation of the process with the particular chemicals just specified, reference is made to the chart shown in the accompanying drawing. In this chart each point represents a group of solutions for which the ratio of fluoride ion : chromic acid used in preparing the solutions is plotted as ordinate against the phosphoric acid used in grams per liter, as abscissa. The cross-hatched area marked "Operative range, good coating" represents the field of compositions within which our novel solutions and process have been found to be operable. The effect of alteration in the proportions of ingredients so that the composition of a solution falls outside the operative range, is indicated by an appropriate description on the chart. Compositions selected as optimum in performance are indicated by the heavy dotted line marked "Optimum line."

Although exact maximum and minimum amounts of fluoride and dichromate to be used in the solutions are difficult to specify, aside from the F:CrO₃ ratio, it has been found generally, that:

1. The fluoride ion content should lie between 0.9 and 12.5 grams per liter, and preferably between 2.0 and 6.0 grams per liter.

2. The dichromate ion content should correspond to a total CrO₃ content of between 3.75 and 60 grams per liter, and preferably between 6.0 and 20 grams per liter.

A good balance between economy in dragged-out chemical, ease of control, and good results

in coating is obtained in the preferred range specified.

Since the essential ingredients of the coating solution are fluoride ion, phosphate ion, dichromate ion, and hydrogen ion, it has been found desirable in making up and replenishing the solution to use concentrated admixtures which need only be added to water or to acidified water to produce operative solutions of the proper composition. Such admixtures have the advantages that:

1. Only one chemical, or at the most two, need to be weighed or measured to make up the solution.

2. Shipping space and weight are saved by the omission of much of the water from the admixture.

3. Errors in calculating and measuring the proportions of the ingredients are minimized, since the proportions are fixed by the composition of the concentrated admixture which can be prepared and checked once and for all.

For making a fresh solution, the concentrated admixture may contain, for example, compounds of fluorine, of phosphorus (as orthophosphate), and of hexavalent chromium, all in a form soluble in water at pH about 2. The composition should contain the constituents in the following proportions:

- 1 part fluorine, by weight
2.47 to 7.40 parts chromium, calculated as CrO_3
2 to 70 parts phosphate, calculated as PO_4

The best compositions should contain, for each part of fluorine, 2.88 to 5.55 parts chromium, calculated as CrO_3 and 7 to 50 parts of phosphate, calculated as PO_4 .

The above admixtures may or may not be compounded to include free acid. The inclusion of acid is desirable from the standpoint of ease in preparing the actual coating solutions, since nothing but water and the concentrated admixture is necessary. However, strong acid solutions containing fluoride and chromate are corrosive and somewhat dangerous to handle. Therefore, acid may be omitted from the composition.

Concentrated compositions may be made up as solutions, slurries, or solids. For ease in shipping and handling solid admixtures are particularly desirable. To get usable coating solutions these need only be added to water, acidulated to the proper degree.

Preferred embodiments of our invention as regards make-up material for the coating solution, embodying only easily obtainable chemicals are as follows:

Formula 7

	Pounds
Sodium fluoride	6.0
Chromic acid (CrO_3)	12.0
Monosodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$)	82.0
	100.0

When the total material of Formula 7 is dissolved in 150 to 300 gallons of water, from 3.0 to 4.3 gallons of 20° Bé. hydrochloric acid will be required to yield a solution in optimum operative condition, depending on the volume of water used.

Another formula for a concentrate, suitable for dilution with about nine times its volume of water

to make a coating solution of optimum quality is the following:

Formula 8

Potassium hydrogen fluoride (KHF ₂)	pounds--	0.158
Chromic acid (CrO ₃)	do--	0.316
Phosphoric acid, 75%	do--	6.667
Water, to make	gallons--	1.000

This material must be stored and shipped in containers suitably corrosion resistant.

No purpose would be served in multiplying the number of such formulas given.

For reasons of cheapness and availability we prefer to use an alkali fluoride or acid fluoride, an alkali chromate, an alkali dichromate, or free chromic acid, and an alkali phosphate or free phosphoric acid in making compositions of this type.

It must be noted that the consumption of fluoride, phosphate, dichromate, and acid during the coating of a succession of surfaces is not usually in the same proportion in which these constituents exist in the solution. In general, the consumption of these ingredients depends somewhat upon the kind and surface finish of the metal treated. The relative rates of consumption of the ingredients are generally about as follows, by weight:

Fluorine, grams	1.0
Chromium, as CrO ₃ , grams	0.7 to 1.4
Acid (gram equivalents of replaceable hydrogen)	0.06 to 0.14
Phosphate, as PO ₄ , grams	0.5 to 1.0

Since the tolerance of the coating solution for variations from the optimum ratio of ingredients is reasonably large, within the limits previously stated, it is possible for limited periods to effect replenishment of the solution with any of the concentrated make-up materials previously described, as, for example, those of Formulas 7 and 8, without failure of the coating process. However, it has been found that if the same solution is to be used for coating a large area of metal, the relative rate of consumption of the ingredients is sufficiently different from their initial relative concentrations so that concentrated admixtures designed for making up the original solution are not capable of indefinitely maintaining the proper ratios of constituents in the working bath.

It has, therefore, been found desirable to prepare admixtures having a ratio of ingredients more nearly like that in which they are consumed. For this purpose compounds of fluorine, of phosphorus (as orthophosphate), and of hexavalent chromium, all soluble in water at about pH 2, are admixed in the ratio shown above, namely, grams, fluorine : grams, chromium (as CrO₃) : grams, phosphate (as PO₄) : 1.0:0.7 to 1.4:0.5 to 1.0.

If the replenishing material is also to contain acid, which must otherwise be added separately, the ratio grams fluorine : gram equivalents of acid (replaceable hydrogen), should be from 1:0.06 to 1:0.14.

An example of a solid replenishing admixture for ingredients of the solution other than the acid is

Formula 9

Potassium fluoride	Pounds	60.6
Chromic acid, CrO ₃		21.9
Monosodium dihydrogen phosphate (NaH ₂ PO ₄ ·H ₂ O)		17.5
Total		100.0

This material is added, as required to maintain the composition and the activity of the solution, along with an acid in sufficient quantity to maintain proper pH and activity.

A liquid replenishing material may also be formulated if desired, for example, as follows:

Formula 10

	Pounds
Hydrofluoric acid, 48%	53
Chromic acid, CrO ₃	29
Phosphoric acid, 75%	18
Total	100

Replenishment of a bath with this material alone usually results in maintaining it in good operating condition for a long time. The above solution, however, is not entirely stable; its rate of decomposition is quite low, however.

For reasons of cheapness and availability we prefer to use an alkali fluoride or acid fluoride, an alkali chromate, an alkali dichromate, or free chromic acid, and an alkali phosphate or free phosphoric acid in making compositions of this type.

It will be seen from the foregoing that in the concentrated admixtures, for each part by weight of fluorine, the quantity of chromium calculated as CrO₃ will range from a minimum of 0.7 part to a maximum of 7.40 parts and that the quantity of phosphorus calculated as PO₄ will range from a minimum of 0.5 part to a maximum of 70 parts for each part by weight of fluorine. It will also be seen that when the admixture is to be used for preparing a fresh solution, the minimum amount of chromium should be 2.47 parts by weight for each part of fluorine and that the minimum amount of phosphorus should be two parts for each part by weight of fluorine and still further that when the concentrated admixture is to be employed in replenishing a used solution the maximum amount of the chromium should be 1.4 parts by weight per part of fluorine and the maximum amount of phosphorus should be 1.0 part for each part by weight of fluorine.

We claim:

1. A process for coating ferrous and zinciferous metals which consists in treating the surface with an acid aqueous solution until a coating is formed; the essential active coating-producing ingredients of which solution are fluoride ion, dichromate ion, phosphate ion and hydrogen ion, the ions being present in amounts stoichiometrically equivalent to

	Grams per liter
Fluorine	0.9 to 12.5
Chromic acid (CrO ₃)	3.75 to 60.0
Phosphate (PO ₄)	2 to 285

the ratio of fluoride ion to dichromate expressed as F:CrO₃, being between 0.135 and 0.405; the pH of the solution being between about 1.6 and 2.2, as measured by the lowest value indicated by a glass-electrode pH meter within the first ten minutes of immersion of the electrode in the solution; and drying the coated surface.

2. The process of claim 1 in which the coated surface is rinsed before drying.

3. The process of claim 1 in which the dried surface is rinsed and then dried again.

4. The process of claim 1 wherein the coating formed is at least partially dehydrated by heating it.

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