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# COMPOSITION FOR TREATING METAL SURFACES

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This application is a continuation-in-part of co-pending United States application Serial No. 232,297, filed October 22, 1962, and now abandoned.

The present invention relates generally to the treatment of metal surfaces to prevent corrosion and discoloration damage thereto and more particularly to a method of treating a galvanied or aluminized metal surface to prevent formation of corrosion or wet storage stains on a galvanized or aluminized surface stored in an atmosphere having a high moisture content and to a composition for so treating a galvanized or aluminized metal surface.

Many methods and compositions for treating galvanized or aluminized steel surfaces, and other metal surfaces to prevent corrosion or "white rust" have been developed in the prior art, but these efforts have either added significantly to the cost of the product or have not been entirely satisfactory, and there is a continuing need for an improved and less expensive treatment for metal surfaces to prevent corrosion, such as the formation of "white rust" on galvanized and aluminized surfaces.

One of the most effective compounds employed for preventing corrosion or wet storage stains on galvanized or aluminized steel or other metal surfaces is chromic acid or alkaline chromate salts. The effectiveness of these compounds is limited by the degree of absorption or retention of the chromic acid or chromate salts on the galvanized or aluminized surface or on the surface of the other metals which are to be protected from corrosion. It is, for example, customary in the art to treat a galvanized surface with a water absorbing compound, such as sodium silicate, to increase retention of the chromate ion on a metal surface and provide a more uniform chromate deposit, as in U.S. Patent No. 2,987,427. The application of sodium silicate or similar silicates on the surface of galvanized sheets, however, is objectionable in a number of instances. For example, silicates interfere with die forming of objects from silicate treated galvanized sheets, and galvanized sheets treated with silicates are not readily painted or bonderized prior to painting. Welding and soldering of the silicate treated galvanized sheets are also hindered or completely prevented by the silicate film.

Various methods and compositions have also been devised by the prior art for depositing a uniform film of chromic acid or chromate ion on a metal surface to be protected against corrosion. In some instances a chromic acid compound is reduced by a compound containing one or more hydroxy groups. None of the presently available treating compositions, however, have been entirely satisfactory for preventing "white rust" formation on a galvanized or aluminized surface exposed for prolonged period to a high humidity atmosphere.

It is therefore among the general objects of the present invention to provide an improved metal coating composition and method of treatment of a metal surface which is simple to prepare, use and apply to galvanized and aluminized surfaces or other metal surfaces subject to corrosion, and which, for example, is usable directly without elaborate or costly preliminary treatment or finishing operations, and which is relatively inexpensive and reduces the overall cost of treating galvanized, aluminized or other metal surfaces.

It is also among the objects of the present invention



to provide an effective corrosion preventive composition and method of treating galvanized, aluminized, or other metal surfaces subject to "white rust" formation thereon which will aid die forming operations, provide an adequate basis for paint adhesion, and provide a surface coating which will aid in fluxing during soldering.

It is a further object of the present invention to provide an effective means for applying a uniform chromate deposit on a sheet metal surface in an economical manner and without interfering with or limiting the principal uses of the said sheet metal.

Other general and specific objects of the present invention will be apparent to those skilled in the art from the following detailed description of the invention and the claims which follow.

In accordance with the present invention it has been discovered that a solution or uniform dispersion of a trialkyl phosphate having from 3 to 8 carbon atoms per alkyl group, including straight or branched chain alkyl groups, such as tri(2-ethyl hexyl) phosphate, has substantial solubilizing action for a hexavalent chromium oxide compound, such as chromic anhydride (anhydrous chromic acid) and forms a composition which when applied to a metal surface readily provides a uniform film of chromium in conjunction with the phosphate on the metal surface and protects the metal surfaces, particularly galvanized or aluminized surfaces, against corrosion and can be prepared to also impart improved secondary properties which are important in the forming and finishing of sheet materials.

More particularly, it has ben discovered that of the known and commercially available organic phosphate compounds, only the trialkyl phosphates wherein the alkyl groups each have between 3 and 8 carbon atoms inclusive, such as tributyl phosphate, triamyl phosphate, trioctyl phosphate, and tri(2-ethyl hexyl) phosphate, have significant solubility for a hexavalent chromium oxide compound, such as chromic anhydride (anhydrous chromic acid). These trialkyl phosphates also have been found to have a marked solubilizing action on boric acid and water soluble salts thereof. Thus, chromic anhydride and boric acid have been found to be solubilized or extractable into tributyl phosphate up to about ten percent (10%) by weight, respectively, at moderately elevated temperatures (105° F.), and at room temperature tributyl phosphate solubilizes or absorbs about eight percent (8%) by weight chromic anhydride and only slightly smaller amounts of boric acid (about 6%) on a weight basis. With the foregoing amounts of chromic anhydride dissolved or absorbed in tributyl phosphate and which preferably also contain dissolved or absorbed boric acid, it is possible to prepare a metal treating composition which permits controlled deposition as a uniform film on a metal surface a chromium composition in effective and economical amounts and also permits imparting to the metal surface treated therewith other desirable properties, including paintability, solderability and lubricity for die formation.

The very significant solubility of chromic anhydride and boric acid in a trialkyl phosphate makes economically feasible and possible the further dilution, dispersion and/or emulsification thereof in a variety of commercially available vehicles or liquid carriers which are chemically inert toward the metal surface to be treated, including both organic and aqueous vehicles. For example, a treating composition comprising tributyl phosphate which contains chromic anhydride or tributyl phosphate which contains both chromic anhydride and boric acid, if desired, can be readily dissolved without impairing the effectiveness of the composition as hereinafter described in such commercially available organic

solvents as naphtha, kerosene, diesel fuel, petroleum oil, gasoline, alcohol, carbon tetrachloride, trichloroethylene, benzene, toluene, xylene, and the like organic solvents or combinations thereof.

In certain applications of a corrosion inhibiting composition of the present invention, it is preferable to use the composition in an aqueous vehicle. And, it has been found that the tributyl phosphate containing chromic anhydride or chromic anhydride and boric acid can be readily dispersed in water by adding thereto an emulsifier, such as a mono-, di-, or tri-alkylolamine, such as monoethanolamine and triethanolamine, or any other of the commonly available wetting agents, detergents, and surface acting agents including the alkyl sulfonate- and aralkyl sulfonate-type emulsifying agents and ethylene oxide condensates.

Whether the composition of the present invention is applied to a surface to be treated from an organic or an aqueous solvent vehicle, a concentration of the tributyl phosphate-chromate solution is used sufficient to provide a concentration of chromium on the treated surface in an amount of at least about 0.25 mg. Cr per square foot and preferably between about 0.75 and 1.0 mg. Cr. per square foot. Satisfactory coating on galvanized or aluminum coated strips using the composition of this invention have been produced having as much as 4.5 mg. Cr per square foot without any evidence of yellow staining which is troublesome with other chromic acid treatments at much lower levels of chromium. No practical or economic advantage is achieved, however, by providing in excess of about 1.0 mg. Cr per square foot in a coating of a galvanized steel strip with the present composition. And, for example, when the treating solution contains about 1% $CrO_3$ by weight (.5% Cr) and about 0.5% by weight tributyl phosphate, the resultant coating deposited on a galvanized steel strip following treatment therewith is found to contain about 1.0 mg. Cr per square foot. The resultant coating also contains a proportionate amount of phosphate, borate and emulsifying agent, if the latter are used in the treating composition. Thus, in the latter embodiment the coating contains about 0.5 mg. tributyl phosphate per square foot and about 0.25 mg. boric acid per square foot.

In general, the chromic anhydride ($CrO_3$) content of the treating composition on a weight percent basis can vary between about 0.1% and 10% by weight and the tributyl phosphate or other trialkyl phosphate between about 0.1% and 99% by weight. And, where boric acid is also included, the formulation of the treating composition on a weight percent basis can vary between about 0.1% and 10% by weight chromic anhydride, 0.1% and 10% by weight boric acid, and 80% and 99% by weight tributyl phosphate. When the treating composition is applied as an organic solvent solution the tributyl phosphate can vary between about 0.1% and 30% by weight, the chromic anhydride between about 0.1% and 10% by weight, and the boric acid between about 0.1% and 5% by weight, with the remainder being a suitable organic solvent.

In the preferred embodiment of the present invention wherein the treating composition is applied as an aqueous solution or emulsion the ingredients thereof can be varied as follows:

| | Range, Percent (by wt.) | Specific Example, Percent (by wt.) |
|---|---|---|
| Chromic Anhydride | 0.1–10 | 1.0 |
| Tributyl phosphate | 0.1–30 | 1.0 |
| Emulsifying Agent | 0.1–30 | 0.6 |
| Boric Acid | 0.1–5 | 0.4 |
| Water | Remainder | |



Whereas the direct combination of anhydrous chromic acid (chromic anhydride) and tributyl phosphate at room temperature results in a combustible mixture, the presence of even a relatively small amount of water with the chromic anhydride enables the chromic acid solution to dissolve smoothly and completely in the tributyl phosphate without oxidation to form a homogeneous stable chelate or complex. It is advisable to employ a chromic acid solution having a minimum concentration of 50% by weight water to prevent an exothermic oxidation reaction, and preferably a somewhat more diluted chromic acid solution (e.g. 20% by weight $CrO_3$) is used when combining the chromic anhydride with the tributyl phosphate to form the homogeneous active complex. It is also possible for the tributyl phosphate which has solubilized or complexed therewith an aqueous chromic anhydride solution to solubilize or absorb therewith an appreciable amount of another metal surface protective or treating agent, such as boric acid or the like. After the homogeneous composition is formed (with or without another treating agent solubilized or absorbed thereby), the homogeneous composition can be diluted with an organic solvent in all proportions or dispersed in water with any conventional emulsifying agent, such as an aralkyl sulfonate, or a lower alkylolamine, or by mechanical emulsifying procedures.

In the various preparations used for treating a metal surface in accordance with the present invention, the treating composition is preferably maintained at a pH above about 2.5 and below about 6, and most advantageously at about pH 5, so that none of the hexavalent chromium is reduced to trivalent chromium even after prolonged standing and use.

The treating compositions of the present invention, while preferably but not necessarily being maintained at a temperature between about 105° F. and 125° F., can be readily applied to a metal surface including galvanized sheets, strips or other articles by dipping, spraying, wiping, rolling, painting or other means of coating, And, while it is generally most conveniently applied to a surface such as a moving galvanized strip by passing the strip through a solvent solution or emulsion of the herein described treating composition or by spraying said solution of emulsion on the galvanized strip, it is also possible to spray the tributyl phosphate containing chromic anhydride and (if desired) boric acid without solvent dilution by means of Grammer sprays.

After application of the treating composition to the surface of an article, such as a continuous galvanized steel strip, by any of the available means, it is generally preferable to contact the metal surface with a wiper or squeegee or the like to insure an even distribution of the solution on the surface of the strip and to remove any excess of the composition. Particularly good results have been obtained by employing wiper rolls fabricated from polyurethane polymer. A greater coefficient of friction between the galvanized strip and the roll is realized with polyurethane wiper rolls than between wiper rolls fabricated from rubber or neoprene polymer; thus overcoming a tendency of the wiper rolls to slip over the surface without turning. And, by coupling a set of polyurethane rolls through a belt or a chain drive to a second set of neoprene or rubber rolls a very uniform film of the treating solution is deposited upon the strip. This coupling of the rolls has also greatly reduced the need for frequent wiper roll changes. After wiping the sheet, the moisture remaining can be removed rapidly by blowing warm air over the surface or by simply allowing the coating to air dry during passage of the strip to a subsequent station.

The following specific examples are given to particularly illustrate the present invention, without, however, limiting the invention to the precise ingredients and proportions used.

*Example 1*

An aqueous tributyl phosphate, chromic acid and boric acid surface treating composition was prepared as herein described and having the following composition:

| | Percent by weight |
|---|---|
| Tributyl phosphate—5 gal. | 1.05 |
| Chromic anhydride—36.36 lbs. | 0.94 |
| Boric acid—13.64 lbs. | 0.35 |
| Monoethanolamine—2.73 gal. | 0.60 |
| Water—diluted to 450 gal. | balance |

Twenty (20) gallons of an aqueous chromic acid solution formed by carefully dissolving 36.36 pounds of chromic anhydride therein are mixed with 5 gal. of tributyl phosphate. The chromic compound is extracted into the organic phase by the tributyl phosphate in the presence of the water without oxidation of the tributyl phosphate and reduction of the chromic compound. To the foregoing is added 10 gallons of an aqueous solution containing 13.64 pounds of boric acid and 2.73 gallons of monoethanolamine. Water is then added to bring the volume of the composition to about 50 gallons. The foregoing ingredients are stirred and complete solubilizing or emulsification is readily effected, whereupon the composition is transferred to a treating tank containing 400 gallons of water and equipped with a recirculating pump.

The foregoing treating composition is maintained at a temperature of between about 105° and 125° F. and is sprayed on both surfaces of a continuously moving strip of galvanized steel. The strip is passed through a pair of oppositely disposed rubber wiper rolls of about 40 durometer hardness to evenly distribute the treating composition and to remove any excess before the strip leaves the treating tank. The pressure of the wiper rolls is maintained so as to provide the desired weight of chromium in the residual coating on the treated surface (i.e. .75 to 1.0 mg. Cr per square foot).

The pH of the treating composition is maintained between the limits of 3 and 6, and preferably as close as possible to pH 5. This can be done conveniently by testing the preparation periodically with suitable test paper, such as pHydrion paper. When the pHydrion paper turns a greenish color, the pH is too highly alkaline, and one quart at a time of aqueous chromic acid solution is added until the pH reaches the desired level. A period of about 15 minutes should elapse between additions of the chromic acid solution. If the pH of the solution is too low, a quart of aqueous monoethanolamine is added in the above manner until the pH again is about pH 5.

At the end of a large scale test run extending over a six day period, the average amount of metallic chromium on the top and bottom surfaces of a galvanized steel strip treated with the foregoing aqueous composition was .92 and 1.27 mg. Cr per square foot, respectively. The pH of the treating composition maintained at an average pH of 5.1 and the chromic anhydride content was maintained at an average weight per cent of 0.99% over the entire run.

The foregoing composition and method of treating when applied to an aluminum coated steel strip imparts very good corrosion resistance which is superior to presently used treatments.

*Example 2*

A slightly modified treating solution was made up as follows: Boric acid ($H_3BO_3$) in an amount of about 17.5 pounds was dissolved in about 30 gallons of water, and to the foregoing was added 6 gallons of tributyl phosphate containing 10% chromic anhydride ($CrO_3$) and 2.5 gallons of monethanolamine ($NH_2C_2H_5OH$). When adding chromic anhydride to tributyl phosphate, at least 50% by weight of water must first be added to the chromic anhydride to enable the extraction of the hexavalent chromium solution into the organic phase and to prevent oxidation of the compound.



Slight stirring of the treating solution will effect complete solubility or emulsification of all of the chemicals which are then transferred to the treating tank containing 400 gallons of water. Thirty-three pounds (33 lbs.) of chromic anhydride are then slowly added to the treating tank and recirculated by means of the recirculating pump.

Following spraying of the solution onto both surfaces of a galvanized steel strip, even distribution and accurate control of the chemical coating was obtained by wiping the strip with a single set of No. 40 durometer polyurethane wiper rolls..

The foregoing chemical treatment provided a residual coating on the galvanized strip which has between 0.8 to 1.0 mg. Cr per square foot. The galvanized steel strips treated in the foregoing manner have been proven by field tests to be equal or superior in resistance to corrosion and surface marking to the more costly two-stage chromesilicate treatment.

*Example 3*

In the same manner described in Example 2, the following weight percentage composition was prepared:

| | Percent |
|---|---|
| Chromated tributyl phosphate | 2 |
| Monoethanolamine | 3 |
| Chromic anhydride | 1 |
| Boric acid | 1 |
| Remainder water. | |

The resulting composition was found to impart good corrosion resistance when applied to a galvanized steel surface.

*Example 4*

In the manner described in Example 1, the following ingredients in the specified amounts were prepared:

| | | |
|---|---|---|
| Triamyl phosphate | gals. | 5 |
| Chromic anhydride | lbs. | 36.36 |
| Boric acid | lbs. | 13.64 |
| Monoethanolamine | gals. | 2.73 |
| Water, diluted to | gals. | 450 |

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

*Example 5*

In the manner described in Example 1, the folowing ingredients in the specified amounts were prepared:

| | | |
|---|---|---|
| Trioctyl phosphate | gals. | 5 |
| Chromic anhydride | lbs. | 36.36 |
| Boric acid | lbs. | 13.64 |
| Monoethanolamine | gals. | 2.73 |
| Water, diluted to | gals. | 450 |

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

*Example 6*

In the manner described in Example 1, the following ingredients in the specified amounts were prepared:

| | | |
|---|---|---|
| Tri(2-ethyl hexyl) phosphate | ml. | 10 |
| $CrO_3$ | g. | 10 |
| $H_3BO_3$ | g. | 4.66 |
| Monoethanolamine | g. | 5.55 |

Water, diluted to 1 liter with water pH 5.0.

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

*Example 7*

In the manner described in Example 1, the following ingredients in the specified amounts were prepared:

| | | |
|---|---|---|
| Tri(2-ethyl hexyl) phosphate | ml. | 10 |
| $CrO_3$ | g. | 10 |
| $HNO_3$—sp. gr. 1.42 | ml. | 5 |

Example 7—Continued

28% $NH_4OH$ ---------- ml-- 15
Kyro E.O. (alkylphenol ethylene oxide condensate) wetting agent ---------- g-- .15
pH 2.5.
$H_2O$ to 1 liter.

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

*Example 8*

In the manner described in Example 1, the following ingredients in the specified amounts were prepared:

Tri(2-ethyl hexyl) phosphate ---------- ml-- 10
$CrO_3$ ---------- g-- 10
$NH_4O_4$ ---------- ml-- 10
Kyro E.O. ---------- g-- .1
pH 4.5.
$H_2O$ to 1 liter.

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

*Example 9*

In the manner described in Example 1, the following ingredients in the specified amounts were prepared:

Tri(2-ethyl hexyl) phosphate ---------- ml-- 10
$CrO_3$ ---------- g-- 10
$NH_4OH$ ---------- ml-- 10
Kyro E.O. ---------- g-- .1
pH 5.0.
$H_2O$ to 2 liters.

The zinc plate treated with the above composition in the standard 40-hour stack test was free of white rust.

In the preceding examples the source of chromic ion in the composition has in each instance consisted of chromic anhydride. It should be understood, however, that a water soluble chromate salt, such as the alkaline chromates including sodium chromate, ammonium chromate, or the like can be dissolved in water and on mixing the chromate solution with the tributyl phosphate or the equivalent triloweralkyl phosphate, the tributyl phosphate will take up the chromate ion to form a homogeneous active complex. Similarly, in place of the boric acid, other borate salts can be used, such as sodium borate, potassium borate, and the like, which yields a boric acid radical in aqueous medium.

It has been found that when an aluminum coated steel strip is treated as described in the foregoing Examples 1 through 9, the same improved corrosion resistance is imparted to the aluminum surface.

While the foregoing specific examples have relied primarily on an alkylolamine as the emulsifying agent, any of the other commonly available emulsifiers and detergents and the like which are generically designated as surfactants can be used in the present invention. For example, among the emulsifying agents which can be used in the present invention are the aralkyl sulfonates, such as dodecyl benzene and tridecyl benzene sodium sulfonates and the aryl sulfonates, such as xylene sodium sulfonate and toluene sodium sulfonate, and lauryl diethanolamide, and lauryl alcohol sulfates. Also usable are the ethylene oxide adducts to fatty and rosin acids, alkyl phenol and its derivatives, the sulfated acrylic nitrogen products and sulfated esters, such as sulfated glycerol monostearate, aromatic sulfonate-oxide condensates, dioctyl ester of sodium sulfosuccinate acid, propylene monostearate, mono and di-glycerides of fatty acids, sulfated alcohol derivatives, polyoxyalkylene esters and sulfonates. It will be evident that there are a great many ionic and non-ionic emulsifiers which can be used in the present invention, and none of the commonly available emulsifiers have interfered with the satisfactory operation of the the present invention when used as described herein.

In the foregoing specification and in the claims appended hereto the term "metal surface" is used to designate the metal surfaces which are readily subject to attack by corrosion, particularly to the formation of a surface discoloration and to the formation of a white surface film commonly designated "white rust," and includes zinc, aluminum, zinc-aluminum alloy, and magnesium surfaces.

Others may practice the invention in any of the numerous ways which are suggested to one skilled in the art by this disclosure, and all such practice of invention are considered to be a part thereof which fall within the scope of the appended claims.

I claim:

**1.** A composition for treating a metal surface susceptible to damage by corrosion selected from the group consisting of zinc, magnesium and aluminum and alloys thereof comprising as an essential active ingredient an aqueous dispersion of between about 0.1% and about 30% by weight tributyl phosphate in combination with 0.1% and about 10% by weight chromic anhydride and with at least a portion of said chromic anhydride being dissolved by said tributyl phosphate, and said tributyl phosphate and chromic anhydride being dispersed in water containing between about 0.1% and about 30% by weight monoethanolamine as an emulsifying agent, and said aqueous dispersion having a pH of between about pH 2.5 and 6.

**2.** A composition as in claim **1**, wherein said aqueous dispersion contains on a weight basis about 1% tributyl phosphate, about 1% chromic anhydride, and about 0.6% monoethanolamine.

**3.** A composition as in claim **1**, wherein said aqueous dispersion contains on a weight basis between about 0.1% and 10% by weight boric acid.

**4.** A composition as in claim **3**, wherein said aqueous dispersion contains on a weight basis about 1% tributyl phosphate, about 1% chromic anhydride, about 0.4% boric acid, about 0.6% monoethanolamine, and the balance of said composition being essentially water.

**5.** A composition for treating a metal surface susceptible to damage by corrosion selected from the group consisting of zinc, magnesium and aluminum and alloys thereof comprising as an essential active ingredient an aqueous dispersion of between about 0.1% and about 30% by weight tri(2-ethyl hexyl) phosphate in combination with between about 0.1% and about 10% by weight chromic anhydride and with at least a portion of said chromic anhydride being dissolved by said tri(2-ethyl hexyl) phosphate, said phosphate and chromic anhydride being dispersed in water containing between about 0.1% and about 30% by weight monoethanolamine as an emulsifying agent, and said aqueous dispersion having a pH of between about pH 2.5 and 6.

**6.** A method of continuous in-line treatment of a surface of an endless strip of metal having a surface selected from the group consisting of zinc, magnesium and aluminum and alloys thereof which comprises; contacting a surface of said strip moving continuously past a treating zone with a fluid aqueous dispersion having as an essential active ingredient a composition comprising between about 0.1% and about 30% by weight tri(2-ethyl hexyl) phosphate and between about 0.1% and about 10% by weight chromic anhydride with at least a portion of said chromic anhydride being solubilized by said tri(2-ethyl hexyl) phosphate to form a solution containing chromate dissolved in said tri(2-ethyl hexyl) phosphate and said aqueous dispersion containing between about 0.1% and about 30% by weight of an emulsifying agent selected from the group consisting of monoethanolamine, diethanolamine and triethanolamine with the balance of said aqueous dispersion being water with said aqueous dispersion having a pH between about pH 2.5 and 6, continuously forming on the surface of said metal strip as said strip moves continuously past said treating zone a uniform wet film containing said solution of chromate and tri(2-ethyl hexyl) phosphorous, and continuously drying said wet film to form a residual dry film containing

chromium in an amount between about 0.25 and about 1.0 mg. per square foot of said metal surface.

7. A method of continuous in-line treatment of a surface of an endless strip of metal having a surface selected from the group consisting of zinc, magnesium and aluminum and alloys thereof which comprises; contacting a surface of said strip moving continuously past a treating zone with a fluid aqueous dispersion having as an essential active ingredient a composition comprising between about 0.1% and about 30% by weight tributyl phosphate and between about 0.1% and about 10% by weight chromic anhydride with at least a portion of said chromic anhydride being solubilized by said tributyl phosphate to form a solution containing chromate dissolved in said tributyl phosphate and said aqueous dispersion containing between about 0.1% and about 30% by weight of an emulsifying agent selected from the group consisting of monoethanolamine, diethanolamine and triethanolamine and with said aqueous dispersion having a pH between about pH 2.5 and 6, continuously forming on the surface of said metal strip as the said strip moves past said treating zone a uniform wet film of said solution of chromate and tributyl phosphate, and continuously drying said wet film to form a residual dry film containing chromium in an amount between about 0.25 and about 1.0 mg. per square foot of said metal surface.



8. A method as in claim 7, wherein said dispersion contains on a weight basis about 1% tributyl phosphate, about 1% chromic anhydride, and about 0.6% monoethanolamine.


**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,224,695 | 12/1940 | Prutton | 252—389 XR |
| 2,732,345 | 1/1956 | Kroenig et al. | 252—389 XR |
| 2,987,427 | 6/1961 | Shaw | 148—6.16 XR |
| 3,160,532 | 12/1964 | Neish | 148—6.16 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 830,839 | 8/1938 | France. |

OTHER REFERENCES

Rose et al., "Condensed Chemical Dictionary" (1961), page 1159 relied on.



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