This invention relates to coated steel members, more particularly to such members which are protected from corrosion.

Among the objects of the present invention is the provision of novel coated steel members which are simple and inexpensive to make and yet are extremely resistant to corrosion.

Additional objects of the present invention include the provision of a novel method for making such members.

The above as well as still further objects of the present invention will be more clearly understood from the following description of several of its exemplifications, reference being made to the accompanying drawings wherein:

Fig. 1 is a partially broken away perspective view of a storage container of the type used to can food articles and the like in accordance with the present invention.

Figs. 2, 3 and 4 are views of further types of articles that illustrate the present invention.

Fig. 5 is a view similar to Fig. 1 of a modified form of storage container embodying the present invention; and

Fig. 6 is a graphical representation of compositions that are suitable for use in the manufacture of cans such as that shown in Fig. 5.

Plain carbon steels such as ordinary SAE 1010 steel, or the conventional Blackplate sheets that are used in the canning industry, are relatively inexpensive and simple to fabricate and use in practically any desired configuration. Unfortunately, these steels are extremely vulnerable to corrosion. In fact, unless the steel is protected as by a film of oil, it will usually corrode even before it can be delivered by the manufacturer to the consumer.

However, by reason of the low cost and extreme versatility of these steels, many different types of treatment have been developed to reduce their corrosion so that their use can be extended to such fields as canning and the like. Perhaps the most widely spread corrosion-resistant treatment is the application of a tin plating. Although the plating of tin has proven to be very satisfactory in most respects, it is fairly expensive and requires in this country that the tin be imported from abroad.

According to the present invention, very effective corrosion resistance can be imparted to members made of the above steels, particularly where these members are to come into body-engaging contact, by applying a coating of an in situ formed combination of hydrated chromium oxides containing about 20 to 60% chromium by weight, about 40 to 95% of the chromium by weight being trivalent, the remainder being hexavalent, and the coating weighting about 10 to 200 milligrams per square foot of surface that is to be protected. The coating is preferably oxidized so that its surface is covered with a film of uniformly adherent iron oxide before the coating is applied.

A can of lubricating oil or roasted coffee beans can have its inner surface covered with the above coating to prevent rusting prior to filling as well as when filled with oil or coffee beans; the outer surfaces of the can can also have the same type of combined chromium oxide coating which provides an excellent substrate for subsequent lithographic coatings, varnishes, lacquers, enamels and other organic coatings.

Instead of applying the coating of the present invention to the can after it is manufactured or after it is filled and sealed, it is simpler to make the can from steel sheets that have the coating applied while they are being produced. This permits the coated sheets to be stored, if desired, and even shipped over substantial distances without requiring any supplemental treatment to prevent them from becoming unmarketable or unsightly as a result of corrosion.

The sheets are readily coated by first making sure they are very clean and then passing them through an aqueous solution of chromic acid and a reducing agent which is compatible with the chromic acid. This compatibility means that the chromic acid and the reducing agent, even though both are present in the solution, will not in the appropriate dilution react rapidly with each other and will not form a visible precipitate while the solution is being contacted with the steel.

The steel sheet wet with the solution is then dried at a temperature above 210° F. During this drying, the chromic acid reacts with the reducing agent and becomes partially reduced. As a result, the final coating is a combination of hydrated chromium oxides containing about 20 to 60% chromium by weight.

An inordinately high degree of corrosion resistance is obtained when 40 to 95% by weight of the chromium in the final coating is in the trivalent condition, the remainder being hexavalent, and the coating itself weighs about 10 to 200 milligrams for every square foot of surface that is to be covered. Coating of this type will give less protection, although coating weights need not be more than about 30 milligrams per square foot to give all the protection that is needed.

If the reducing agent is omitted from the coating bath, dried coatings of the above weight range will not show the desired trivalent chromium content. They also tend to be somewhat deliquescent and therefore inferior.

Typical reducing agents suitable for use in connection with the present invention are organic polyalcohols such as sugars, including invert sugar, sucrose, dextrose, glycerol, and polyethylene glycols, glycercine, mannitol, sorbitol, triethanolamine, hydroxylamine as well as its salts such as its sulfate and hydrochloride, phosphorous acid, and potassium iodide.

Care should be taken to limit the amount of water-soluble material that is included in the coating. Although as much as 5 or 6% of such materials can generally be tolerated, it is preferred to use reducing agents that do not leave such materials in the final product. Potassium iodide is not a preferred type of reducing agent inasmuch as it is carried through as water-soluble potassium compounds after reducing the chromic acid. Phosphorous acid is a better reducing agent even though it is oxidized to phosphoric acid because the drying operation converts such phosphoric acid to water-insoluble phosphates.

The most effective reducing agents appear to be the organic polyalcohols since their oxidation products are essentially completely volatilized and driven off during the drying operation.

As indicated above, the coatings of the present invention are preferably applied to a steel that has had its surface covered with an oxide film. The oxidation need not be extensive and can be accomplished by etching which may vary from an insignificant amount to a heavy etch that removes 100 to 1000 milligrams of metal per square foot of steel surface. The oxidation can be effected by merely attacking the surface with a reagent that converts it to oxide with substantially no removal of metal. The etch type of treatment can be expected...
by contacting the steel surface with aqueous nitric acid having a concentration of from 1 to 20% HNO₃ by weight for a period of from 2 to 70 seconds at a temperature of from 60 to 150°F. This treatment appears to be achieved by an etching film. Aqueous solutions of ammonium persulfate, picric acid or ferric nitrate are also effective and react similarly to nitric acid solutions. For example an aqueous solution containing 4% of ammonium persulfate will, when applied at 75°F. for 15 seconds remove approximately 380 milligrams of metal per square foot and provide a very satisfactory surface for the chromium oxide coating. A 15% picric acid solution in water at 155°F. for 12 seconds removes about 370 milligrams of metal per square foot and also leaves an excellent pretreatment surface. The nonetching type of oxidation can be accomplished with hot concentrated aqueous solutions of sodium hydroxide containing sodium nitrate as used in standard bluing operations. A concentration of 39% NaOH and 2% NaNO₃ used at 280°F. is very effective although any bluing treatment applicable.

It is not desirable to have oxide pretreatment films that are loose or non-adherent; the oxide produced should be continuous and adherent to the metal surface. However, such films as ordinary corrosion do not interfere with the application of the coating since loose portions are readily removed as by a conventional pre-cleaning operation.

The proportion of reducing agent to chromic acid should be insufficient for the complete reduction of all the chromic acid to trivalent condition. The minimum amount of reducing agent is that below that which will stoichiometrically reduce the lowest proportion of the chromium, inasmuch as some of the chromium is reduced during the drying operation even if the reducing agent is not present in the bath. Chromic acid solutions of any concentration can be used and the coating weight adjusted by controlling the amount of solution that is left on the metal surface when it is being dried.

The final heat treatment is somewhat more effective if carried out at temperatures substantially above 212°F. Temperatures between 250°F. and 500°F. are preferable, and provide the most corrosion-resistant and adherent forms of coating. At about 450°F. and higher, however, the coating appears to be adversely affected.

Referring now to Fig. 1, there is shown a can 10 representing one embodiment of the present invention. The can has a tubular body 12 made in the conventional manner from a single strip of a full bright finished steel 10 mils thick with the ends joined together as indicated at 13. These ends are folded back on each other to provide interlocking flanges 16 and 18 between which a yielding gasketing layer 17 such as rubber is applied. The flange and gasket combination is then crimped together to make a suitably sturdy and leak-proof joint.

The opening at the top and bottom of the tubular body are sealed with covers 20, 22 that have beaded peripheries 24 with interlocking flanges 26, 28. The interlocking beaded periphery can merely be crimped, preferably with a layer 30 of gasketing to assure hermetic sealing.

As shown by the broken-away edge 32, the metal of the body has a coating 34 applied in accordance with the present invention. This coating was provided on the unfabricated sheet by subjecting it to the following operations:

A. Clean the Blackplate cathodically in an aqueous solution containing 16 grams KOH per liter using a current density of 15 amperes per square foot of cathode at 140-160°F. for 10 seconds.

B. Cold water rinse.

C. Clean anodically in an aqueous solution containing 16 grams KOH per liter using a current density of 15 amperes per square foot of anode at 140-160°F. for 10 seconds.

D. Cold water rinse.

E. Flood oxide passivity-preventing ½% aqueous H₂SO₄ solution by a weight 1–2 seconds at 80°F.

F. Cold water rinse.

G. Spray with an aqueous solution containing 2% nitric acid, 80°F, 8 seconds using a spray pressure of about 6 pounds per square inch.

H. Cold water rinse.

I. Desmut by brushing in water to remove loose or non-adherent reaction products including any developed in G.

J. Flood with an aqueous solution containing 4% chromic acid and 1.3% cane sugar at 75°F. for 2 seconds.

K. Roll through rubber rolls wetted with the flooded solution.

L. Cure by passing the resulting filmed metal through a drying unit having a set of ceramic gas burners heated red hot by burning gas, a five second exposure to the incandescent units being used, and the metal reaching a temperature of 300 to 350°F. If the metal is in the form of an elongated strip, it may be coiled up directly after step L.

The same coated sheet can be used for making both the top and bottom covers 20, 22 as well as the body 12 of Fig. 1, although in some cases different thicknesses of metal can be used in the different portions, so that separate coated sheets are required.

After the can body is secured together in the above manner, or by soldering, the cover on one end can be applied in any convenient manner such as the one generally used in the industry and shown in Fig. 1. The can can then be filled and the remaining cover applied with the usual precautions in the case where the contents have to be sterilized or heated, or kept in a special atmosphere such as under evacuation or superatmospheric pressures. The cans having the coatings of the present invention are particularly useful in storing such materials as dried foods, nuts, spices, dough mixtures, etc., as well as the above-mentioned coffee and lubricating oil. Wet-packed foods or other materials can also be stored in the cans of the present invention, but here it is desirable to have an organic covering layer (enameled, lacquered, varnished) applied over the coating of the present invention on the inside surface of the can.

The coatings of the present invention contributed a substantial amount of increased adhesion and wear resistance for such organic type coatings as described previously. Suitable organic layers are those usually loosely referred to in the art as enamels, sanitary enamels or lacquers such as the oleo-resinous phenolic or vinyl resin varnishes. Particularly effective forms of such organic type coating are described in U. S. Patents numbered 2,231,407, 2,299,433, 2,479,409 and 2,675,354. Such top coatings will even further reduce corrosion as well as increase the wear resistance and lower the contamination of the can contents by the oxides.

According to another phase of the present invention, the advantageous characteristics contributed by the inorganic coating of the present invention can also be used for machine elements, particularly those that come in contact with the body and have a tendency to be corroded by perspiration that they thereby pick up. Such metal members as the external portions of firearms, pistols, rifles and metal camera bodies, for instance, are very advantageously given the above type of coating. This not only increases the life of the parts upon handling but in addition improves the ease with which the parts slide on each other upon the addition of a slight amount of oil for example. In fact, the improvement in sliding action makes the oil-coated coating desirable for use even
on the internal portions of mechanisms where they are not subjected to be handled.

Fig. 4 shows an embodiment of this phase of the invention. Here a rifle 80 has its exposed body-engaging parts, including trigger 81, trigger guard 82 and barrel 83 covered with a hydrous mixture of chromium oxides as described above. This coating is particularly effective if applied directly over a surface that has been blued in the conventional manner.

The advantages of the present invention are contributed to any plain carbon steel that is steel that can be no more than about 2% of alloying metals. They can have a carbon content varying from extremely low values, 0.05% or even less, to as much as 1.4% or higher. The phosphorus and sulphur contents can range from substantially zero up to several tenths of a percent. Generally phosphorus maxima are about 0.15% and sulphur maxima about 0.3%. These materials include the steels ordinarily considered as carbon steels (SAE 1010 to 1095), free cutting steels, plain carbon tool steels, including those that have up to several percent of silicon, and cast iron.

The inorganic mixed chromium oxide coating of the present invention is even further improved if after the final high temperature drying it is subjected to a quench that rapidly reduces its temperature at least about 25° F. Any liquid appears to be suitable for this purpose, and tap water or very hot water is very effective. The addition of 0.03 to 1.0% CrO₃ in the quenching water even further improves its effectiveness.

The mixed chromium oxide is also improved by including with these oxides a small amount of an oxide of a metal such as molybdenum that is in the same periodic group as chromium. Such supplemental oxide can be added to the chromic acid bath as water-soluble oxides, acids, or as water-soluble salts. It is preferred to add molybdenum as MoO₃. The advantages of the supplemental oxides are felt when they make up as much as ½ the weight of the final coating, although it is preferred to use from 5 to 20%. The combined oxide coatings show particularly good adhesion to the steel with or without a previous oxidation, as well as better adhesion to an organic top layer. Similarly reducible compounds of either metal such as titanium and vanadium can also be used. In general, it is desirable to diminish the proportion of reduced chromium oxide in the final coating, when a supplemental oxide is used, to not over approximately 75%. The addition of 1 to 5% of insoluble or slightly soluble chromate of such divalent metals as zinc, calcium and strontium also improves the quality of the coating in a similar manner. This effect is obtained with or without the supplemental oxide.

The improvements contributed by the quenching as described above are also produced with the coatings that have the supplemental oxides, or the slightly soluble chromates, or both.

The above coating techniques can be readily carried out either in a batch process or continuously. They may, for example, be added at the end of a standard sheet steel production line. In fact, the coating treatment of the present invention can be carried out with the steel moving at a relatively high speed through the necessary treating stations. Under some condition, particularly where the steel is moving very rapidly through a chromic acid bath, it is desirable to have a wetting agent present in the bath. This enables the bath liquid to more rapidly and uniformly wet the surface of the metal. Wetting agents of any type can be used so long as their wetting action is not completely destroyed by the oxidizing action of the bath. Anionic, cationic, and non-ionic types of wetting agent used in amounts of about 0.001 to 0.1% by weight of the bath is effective to keep from developing coating irregularities apparently due to air bubbles trapped on the metal while moving through the chromic acid bath. A highly effective example of wetting agent is the polyoxyethylene ether of alkylated phenols such as those produced by condensing dodcyl phenol with twelve molecules of ethylene oxide. Reference is also made to U. S. Patents 1,970,578 and 2,085,706 for more specifically disclosed wetting agents that are suitable.

The oxide-coated steel of the present invention is further protected against corrosion by applying to the coating a film of an oil such as a paraffin or a glyceride oil. Thus mineral oil or palm oil can be applied in very minute quantities (0.5 milligram or more per square foot) as by conventional electrostatic coating techniques and enhances the corrosion resistance of the oxide coatings as well as reduces friction to simplify fabrication operations such as stamping, bending etc.

Under some conditions the nitric acid treatment of the steel does not produce the desired effect unless the steel is subjected to a preliminary activation. Under these conditions the steel appears to be passive, and any chemical attack as by very dilute sulphuric acid or even mechanical working of the steel will suffice to activate it. The addition of ¼ to 2% urea to the nitric acid bath tends to suppress NO formation thereby reducing the tendency for iron to be oxidized to ferric form. The urea is consumed in the process and can therefore be replenished either on a continuous basis or by infrequent additions.

In commercial operations large quantities of dissolved iron will build up in the nitric bath with a consequent increase in specific gravity of the bath. If the iron content becomes too high excessive drag-out results and in addition there is an increased tendency for oxidation of ferrous iron to ferric iron. It is preferred to permit the iron content to build up to no more than about 100 to 120 grams per liter, although very effective coatings are obtained if these limits are exceeded. It is desirable to either continuously or intermittently remove and replace a portion of the bath. The removed portions of the bath are advisedly treated to recover the nitric acid and nitrate content. One desirable procedure for doing this is by adding an excess of lime to the exhausted bath to precipitate out the iron as insoluble hydroxide, which is filtered off. The filtrate can then be acidified with sulphuric acid and boiled to drive off the nitric acid which is distilled over and collected. If desired, the sulphuric acid acidification can be effected merely to the neutralization point and the precipitated calcium sulfate filtered off to leave a nitric acid solution that can be reused that can be directed to distillation. The small amount of calcium sulfate that remains in the solution in the filtrate can be further minimized by conducting the filtration at high temperatures where the solubility of calcium sulfate is diminished.

As stated previously etching and oxidizing with HNO₃ can be effected with concentrations of HNO₃ from 1 to 20% and temperatures from 60 to 150° F. Not only is it desirable from a handling and economic standpoint to work with low concentrations of HNO₃ (less than 5% by weight) and low temperatures (less than 110° F.) but extremely advantageous from a standpoint. The lower concentration and temperature provide somewhat more uniform results and greatly minimize the tendency for oxidation of ferrous iron to ferric iron. It should be noted that this oxidation consumes excessive amounts of nitric acid and is accompanied by the generation of large quantities of oxides and oxides of nitrous oxide fumes.

Figs. 2 and 3 show other articles with which the invention is very effective. The article of Fig. 2 is a stamped metal toy as manufactured in large quantities for children's playthings, from ordinary SAE 1010 steel. Articles made in this way are conventionally covered by a protective layer of paint to keep them from corroding when they are handled. Many articles of this type have the protective layer applied in various colors arranged to stimulate articles such as automobiles, airplanes, etc.
Since these articles are expendible and made as inexpensive as possible, the protective layer is generally applied to the steel before the blanking operation and as well as any assembling where this is necessary. Any blanked out or cut edges of the stamping are therefore not coated and likely to corrode. In addition the protective layer is applied to the film, with adherent oxide if desired, and the chromium oxide coating can also be improved by the inclusion of supplemental oxide or any of the other described techniques. The use of the invention in this type of article reduces the tendency for corrosion to take place and therefore increases the inhesion of the external film of paint or the like.

Fig. 3 shows a Venetian blind slat made of steel and covered with the chromium oxide coating of the present invention, in any of its forms. Since these slats are generally required to be of relatively springy nature, the steel from which they are made can be given an extra severe rolling operation or can have a higher carbon content. High carbon steels are usually more susceptible to corrosion than the low carbon steels, and coatings of the present invention are highly effective to prevent this corrosion. These coatings can be applied either before or after the slat is blanked out insuch as the protection of any cut edges is not too significant. Paint or other protective layers are preferably applied after the coating and the final product, will not show corrosion for several years in normal use. Any cut edges not covered by the chromium oxide coating should be covered by paint.

Inasmuch as the chromium oxide coatings of the present invention show unusually high resistance to chemical attack, soldering to such coated metal is made somewhat difficult. Not only is it necessary to use special flux, but even then the removal of the coating to permit access of the solder is a relatively slow process. It is, therefore, preferable and certainly more rapid to make can seams by crimping rather than with the gasket, indicated above. This gasket can be either pre-formed or can be applied as a coating of resin or the like in cured or uncured form, for example. Where an uncured layer is used, aging or heating can be used to effect a partial or complete cure.

Enlarged there is a can similar to that of Fig. 1 but joined with a soldering operation as referred to above. The can 10 is shown with its components identified by the same reference characters used in Fig. 1 where applicable. However, in the construction of Fig. 5 the strip of metal joining the body has its flanged ends joined by soldering as indicated at 14. Soldered joints can also be used to seal the can ends if desired.

The can body of Fig. 5 can be soldered together after being blanked to shape, by dipping the edges to be joined first in a flux and then in a bath of molten solder. This causes the flux to attack the coating and permits the solder to wet the immersed metal over the area of the joint. The solder-carrying edges are then washed as with water to remove residual flux, and the resulting sheet fed to a can-forming machine where the solder-carrying edges are joined to form interlocking flanges 16, 18, and these edges are crimped together and subjected to a heat treatment to liquify the solder and hermetically seal the joint.

Suitable fluxes for the above purposes are mixtures of hydrochloric acid and ammonium chloride. Neither of these ingredients by themselves is suitable, but when mixed in certain proportions they will together provide the necessary fluxing action. The more concentrated the hydrochloric acid the less ammonium chloride is needed. At extreme dilutions the acid will, however, not be suitable regardless of the proportions of the ammonium chloride that is added.

Fig. 6 indicates the effective range of flux formulations with tin-lead type solder. In this figure, curve 50 represents the range of hydrochloric acid concentrations with the minimum proportion of ammonium chloride that will be suitable. Thus, point 51 on this curve represents a hydrochloric acid concentration of 35%, that is a solution of 35 grams of dry hydrogen chloride in 65 grams of water. At this concentration the acid requires the addition of 0.15% of ammonium chloride by weight.

In other words, for each 100 grams of the concentrated acid, 0.15 gram of ammonium chloride is added. The ammonium chloride dissolves in the hydrochloric acid so that the final mixture is a clear solution.

As indicated at point 52, when the hydrochloric acid concentration drops to 17.5% by weight the minimum ammonium chloride addition is 0.26%. Point 53 represents 7% hydrochloric acid, at which concentration 0.42% ammonium chloride is needed. As the acid concentration drops toward 3%, which approximates the minimum that is effective, the ammonium chloride proportion increases sharply. At 4% hydrochloric acid (point 54) for example, 1.5% ammonium chloride is needed.

The above mixture can also have their ammonium chloride content increased without affecting the fluxing action to any appreciable degree. In Fig. 6 there is accordingly indicated a shaded area 60 which represents the above formulations with the excess ammonium chloride that can be added. For convenience, the excess ammonium chloride is desirable since it reduces the criticality of the flux formulation. Sufficient excess ammonium chloride can be added to make a solution saturated with respect to this ingredient. If desired, even more ammonium chloride can be present, in which case it should not be present in such amount as to keep the flux from losing its fluid character. In view of the above, the upper limit of ammonium chloride formation has not been sharply defined in Fig. 6. For practical purposes it can be considered as that amount which will dissolve in the acid.

Although a 35% hydrochloric acid makes a suitable flux ingredient, as indicated above, it is usually desirable for commercial operations to use an acid that is no higher than about 25 to 30%. This reduces the amount of hydrogen chloride fumes that are evolved by the flux and makes it simpler to handle with less precautions needed to keep hydrogen chloride fumes from being spread around and attacking metal or other materials or personnel that might be near by. This is particularly important when the flux-containing metal is dipped into the fused solder bath, inasmuch as the temperature of this treatment is more likely to cause the liberation of hydrogen chloride fumes.

The soldering of the body can also be effected after the joint is prepared by fancying and interlocking the flanges 16, 18. The flux and hot solder is in this case applied to the joint area after the interlocking, and the washing off of excess flux can be accomplished immediately afterward or subsequent to the can sealing.

The coatings of the present invention can be applied to articles after they are formed as by shaping, stamping, or even casting. When treating such formed articles with the liquid coating solutions, however, care should be taken to see that the layer of solution on the article does not concentrate as by running or dripping to any portion of the article that should be protected. A localized thick layer of solution tends to form on the lower, or toward the edges of an article under the influence of gravity, but a blast of air can be used to redistribute the thick layer. Alternatively, the articles can be rotated or kept moving so as to keep a thickened film from forming at any location.

Although it is indicated above that coating weights of at least ten milligrams per square foot are required to
give the exceptional corrosion resistance for some purposes, such as to anchor organic covering layers, coatings of somewhat lower weight will provide unusually good results.

This application is a continuation-in-part of Serial No. 277,286, filed March 18, 1952, Serial No. 278,481, filed March 25, 1952, and Serial No. 371,427, filed July 30, 1953.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. A storage container having walls of plain carbon steel covered with an in situ formed adherent iron oxide surface film, the film being coated with an in situ formed combination of hydrated chromium oxides containing about 20 to 60% chromium by weight, about 40 to 95% of the chromium by weight being trivalent, the remainder being hexavalent and the coating weighing about 10 to 200 milligrams per square foot of surface that it covers.

2. A plain carbon steel container having a corrosion-inhibiting coating of an in situ formed combination of hydrated chromium oxides containing about 20 to 60% chromium by weight, about 40 to 95% of the chromium by weight being trivalent, the remainder being hexavalent, and the coating weighing about 10 to 200 milligrams per square foot of surface that it covers.

3. The container of claim 2 in which the coating is covered with an organic protective layer.

4. The invention of claim 2 in which the coating also includes uniformly distributed through it about 5% of combined metal of the class consisting of zinc, calcium and strontium.

5. The invention of claim 2 in which the coating also includes uniformly distributed through it up to about one-third its weight of molybdenum oxide.

6. A plain carbon steel container having a corrosion-inhibiting coating of an in situ formed combination of hydrated chromium oxides containing about 20 to 60% chromium by weight, about 40 to 95% of the chromium by weight being trivalent, the remainder being hexavalent, the coating weighs about 10 to 200 milligrams per square foot of surface that it covers and the surface of the steel under the coating being nitric acid etched.

7. Plain carbon steel having its surface coated with an in situ formed combination of hydrated chromium oxides containing about 20 to 60% chromium by weight, about 40 to 95% of the chromium by weight being trivalent, the remainder being hexavalent and the coating weighing about 10 to 200 milligrams per square foot of surface that it covers.

8. The invention of claim 7 in which the steel surface underneath the coating is nitric acid etched.

9. The invention of claim 8 in which the coating also includes uniformly distributed through it about 5% of combined metal of the class consisting of zinc, calcium and strontium.

10. The invention of claim 8 in which the coating also includes uniformly distributed through it up to about one-third its weight of molybdenum oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,067,214 Tanner et al. .......................... Jan. 12, 1937
2,288,182 Curtin ............................... June 30, 1942
2,301,983 Tanner ............................... Nov. 17, 1942
2,303,242 Tanner et al. ........................ Nov. 24, 1942
2,314,565 Thompson ............................ Mar. 23, 1943
2,393,663 Thomas et al. ........................ Jan. 29, 1946
2,535,794 Hempel ............................. Dec. 23, 1950

FOREIGN PATENTS

597,754 Great Britain ......................... Feb. 23, 1948

OTHER REFERENCES

Steel, page 87, issue of February 26, 1945.