United States Patent Office 3,472,681 Patented Oct. 14, 1969

3,472,681

PROTECTIVE COATED ASBESTOS CEMENT PANELS

Ludwig K. Schuster, Dresher, and Alfonso L. Baldi, Jr., Drexel Hill, Pa., assignors to Pennwalt Corporation, a corporation of Pennsylvania

No Drawing. Continuation-in-part of applications Ser. No. 222,864, Sept. 11, 1962, and Ser. No. 282,571, May 23, 1963. This application July 28, 1966, Ser. No. 568,377
Int. Cl. B44d *1/34;* C08f *45/26*
U.S. Cl. 117—126 3 Claims

ABSTRACT OF THE DISCLOSURE

Asbestos cement panels and other articles such as corrodible metals have surfaces protected by coating cured from a layer of aqueous dispersion of resin containing chromic acid or water-soluble dichromate of metal having valence greater than one, and also containing reducing agent that causes 40 to 95% of the chromium to be reduced to trivalent condition when layer is dried and heated above 212° F. Dispersion can also contain pigment. Dispersion can be prepared from a concentrate or from mixture of dry chemicals.

The present application is a continuation-in-part of applications Ser. No. 222,864 filed Sept. 11, 1962 (now U.S. Patent 3,318,716 granted May 9, 1967) and Ser. No. 282,571 filed May 23, 1963 (now U.S. Patent 3,346,552 granted Oct. 10, 1967), both of which are in turn continuations-in-part of application Ser. No. 6,021, filed Feb. 1, 1960 (now U.S. Patent 3,128,546 granted Apr. 14, 1964), Ser. No. 88,018 filed Feb. 9, 1961 (now U.S. Patent 3,094,435 granted June 18, 1963), and Ser. No. 108,130 filed May 5, 1961 (now abandoned). Application Ser. No. 88,018 is also a continuation-in-part of application Ser. No. 708,772 filed Jan. 14, 1958 (now abandoned).

The present invention relates to the coating of materials to protect them from the weather or other deleterious influences.

Among the objects of the present invention is the provision of novel compositions for preparing the above coatings, as well as novel coated articles.

The above as well as additional objects of the present invention will be more fully understood from the following description of several of its exemplifications.

The above-mentioned prior applications describe the coating of materials such as corrodible metals, particularly plain carbon steels such as SAE 1010 steel, with an in situ formed combination of hydrate 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, and in some cases as little as one milligram per square foot, of surface that it covers. As disclosed in application Serial No. 592,552 filed June 20, 1956 (now U.S. Patent 3,031,333 granted Apr. 24, 1962), such plain carbon steels, if given a grain-boundary etch before coating, show much greater corrosion resistance.

A can for liquid detergent, lubricating oil, coffee beans, or the like, can have its inner surface covered with the above coating to prevent rust prior to filling as well as after filling with the above materials; the outer surfaces of the can can also have the same type of combined chromium oxide coating inasmuch as it provides an excellent substrate for subsequent lithographic coatings, varnishes, lacquers, enamels and other organic coatings.

Instead of applying the foregoing coatings to a 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 212° 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.

And inordinately high degree of corrosion resistance is obtained when 40 to 95% by weight of the chromium in the final coating is in what corresponds to the trivalent condition, the remainder being hexavalent, and the coating itself weighs about 10 to 100 milligrams for every square foot of surface that it covers. Coatings of less weight 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 the above-described use are organic polyalcohols such as sugars, including invert sugar, sucrose, dextrose, glycol and polyethylene glycols, glycerine, mannitol, sorbitol, triethanolamine, hydroxylamine salts such as its sulfate and hydrochloride, phosphorous acid, and others such as the aluminum lactate mentioned in application Ser. No. 738,648 filed May 29, 1958 (now U.S. Patent 3,053,693 granted Sept. 11, 1962). The preferred reducing agents are those like the polyalcohols which are oxidized by the chromic acid without leaving water-soluble reaction products. Phosphorous acid is oxidized to phosphoric acid by the chromic acid, and by reacting with the surface of the coated metal, the phosphoric acid is converted to phosphates that are insoluble in water.

The proportion of reducing agent to chromic acid should be insufficient for the complete reduction of all the chromium to trivalent condition. The minimum amount of reducing agent is somewhat below that which will in a body of solution 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 almost 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. However, concentrations of from about ½ to about 30% CrO_3 are most readily used.

The final heat treatment is somewhat more effective if carried out at temperatures substantially above 212° F. Temperatures between 275° F. and 450° F. are preferable and provide the most corrosion-resistant and adherent forms of coating. At about 500° F. and higher, however, the coating appears to be adversely affected unless the exposure to that temperature is held down to about two seconds or less.

The same coated sheet can be used for making both the top and bottom covers as well as the body of a can, although in some cases different thicknesses of metal

can be used in the different portions, so that separate coated sheets are required.

The above coating can be readily applied either by a batch process or continuously. It may, for example, be added at the end of a standard sheet steel production line. In fact, the coating can be effected with the steel moving at a relatively high speed through the necessary treating stations. Under some conditions, 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 or nonionic types of wetting agent used in amount of about 0.001 to 0.2% by weight of the bath are 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 that produced by condensing dodecyl phenol with twelve molecules of ethylene oxide. Reference is also made to U.S. Patents Nos. 1,970,578 and 2,085,706 for more specifically disclosed wetting agents that are suitable.

One example of the coating process of the present invention is as follows:

EXAMPLE I

(A) Sheets of 14 mil thick SAE 1010 steel are cleaned by immersing for five seconds in a 180° F. aqueous solution of 5% disodium phosphate and 3% sodium carbonate.

(B) The cleaned sheets are rinsed with water at 70° F.

(C) Immerse the rinsed sheets in 1/10% solution of sulfuric acid in water for one second at 70° F.

(D) Rinse in water at 70° F.

(E) Subject the resulting sheets to a uniform action of jets of an aqueous solution containing 1.2% nitric acid at 80° F. for two seconds, the jets impinging at a velocity of ten feet per second.

(F) Rinse the acid treated sheets in cold water at 70° F.

(G) Pass the sheets between rotating brushes having strainless steel bristles, to remove loose material.

(H) The rinsed sheets are sprayed with an aqueous solution of 3½% chromic acid, 1% pentaethylene glycol and 0.1% of the wetting agent made by condensing 3 mols of ethylene oxide with p-(n-octyl) phenol. This solution was prepared in the mixing nozzle by supplying it with two separate streams, one being an aqueous solution of the chromic acid, and the other an aqueous solution of the remaining ingredients.

(I) The sheets carrying the above solution are passed through an air oven, the inside of which is held at 800° F., the surface of the sheets reaching a temperature of 375° F.

(J) The hot sheets are quenched with water at 70° F., and then permitted to dry.

The dried product is extremely resistant to corrosion, particularly if coated with an acrylate lacquer or even a thin film of methylmethacrylate resin. Other resins such as those made with ester-type waxes, carnauba wax for example, are also very effective.

The mixed chromium 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.

Joints in cans or the like made of steel or other soldered metals coated with the mixed chromium oxides of the present invention, can be sealed by soldering as described in parent application Ser. No. 6,021.

Soldering is also a good way to seal joints in metal cans or the like where only one surface of the metal carries the mixed chromium oxide layer of the present invention. For example, a dog food can may have its internal surface tinned and its external surface coated with such oxide layer. The flux treatment described in Ser. No. 6,021 does not affect the tinned surface so that the attraction of the tin to solder helped in the soldering. The inside and ouside surfaces of such a container can also be interchanged, but in either case it is helpful to apply an organic coating over the tin and/or the mixed chromium oxide coating, to improve their characteristics.

The soldering of container joints is helpful in that the solder covers and further protects the portions of the container walls that are crimped together to make the joints. Such crimping can be quite severe and can subject the metal to so much distortion as to fracture or loosen the mixed chromic oxide coating, particularly if the coating is relatively heavy. Soldering at a joint over such severely deformed metal will fully protect the metal against corrosion.

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 concenrate 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 edges of the 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.

The coating solutions for the present invention need not be prepared from separate chemicals which have to be carefully combined in the proper proportions by the final compounder. It is a feature of the present invention that the dry or concentrated chemicals can be mixed in the proper proportions and shipped as such a mixture for use in the coating operation. Such mixtures are more readily shipped since they take up less room and are not encumbered by large quantities of water. Furthermore, dry mixtures containing CrO_3 can be stored indefinitely and are much more stable than solutions.

This stability is an unexpected characteristic of mixtures of CrO_3 and sucrose, for example. When these materials are mixed together in perfectly dry condition they show no tendency to react, notwithstanding the fact that when in dissolved form these two materials react with each other more and do this more violently as the concentrations of the solutions increase. The regular commercial grades of these materials have moisture contents less than 0.1% and can be directly mixed, and the resulting mixture placed in a conventionally sealed container such as capped bottles or even paint cans with friction covers. The mixing need not be such as to produce a uniform mixture, although uniformity is readily obtained and is desirable where the entire contents of a single container need not be used at one time. However, the mixing itself should be carried out under conditions of low relative humidity or with only limited exposure to high humidity in order to keep the CrO_3 from absorbing too much moisture.

To use the prepared dry mixture for coating it is only necessary to drop the contents into a sufficiently large quantity of water preferably with stirring, so as to prevent local high concentrations that can cause reaction. As soon as the solids are completely dissolved, the solution is ready for use. If undissolved material is present in the solution, it is preferably filtered before use.

Any of the above-mentioned water-soluble reducing agents that are solid will, when substituted for the sucrose, also be stable in the above mixtures and can be similarly used in conjunction with the present invention. All these reducing agents are compatible with a 4% water solution of CrO_3 for at least one day at 80° F., but react with the CrO_3 in films of said solution at temperatures above 212° F. to cause reduction of from about 40 to 95% of the chromium in the CrO_3 to trivalent condition. The proportions of the ingredients can be from 3 to 5 parts by weight of CrO_3 as against from 1 to 2 parts by weight of the solid water-soluble reducing agent.

In accordance with the present invention the above dry mixtures can be further improved by including in them oxides or carbonates of metals such as zinc, magnesium, aluminum and calcium in a proportion up to that which is stoichiometrically required to form a dichromate with the CrO_3. Such addition acts to dilute somewhat the dry concentration of the CrO_3, and thereby further safeguards the stability of the dry mixture, should the mixture for example be inadvertently exposed to high humidity. Furthermore, these additions, particularly when sufficient to actually reach the stoichiometric proportion, greatly stabilize the coating solution that is eventually formed from the dry mix, all without detracting from the efficacy of the final coatings.

As an example of the above dry mixes, there can be combined 3 parts by weight of CrO_3, one part by weight of sucrose, and 1.2 parts by weight of ZnO. The CrO_3 is in the form of a powder that just passes through a 150 mesh screen, the sucrose is in the form of ordinary granulated sugar as supplied to the grocery market, and the ZnO as a +250 mesh powder. The ZnO can first be mixed with the CrO_3, after which the sucrose is added to give the final blend which can be stored for several years if necessary. Upon pouring into sufficient water to provide a solution having 3% CrO_3 by weight, an effective coating solution is prepared. In some cases a small amount of normal zinc chromate, insoluble in the solution, is also formed and it is desirable to decant or filter the solution away from such residue.

Instead of the above dry mixtures, a pre-prepared dichromate can be mixed with the reducing agents of the present invention. Strontium dichromate is an example of such a dichromate, and can be readily prepared as coarse crystals about ⅛ to 1/16 inch in size. In general, water-soluble dichromates of metals having a valence greater than 1, such as the dichromates of zinc, magnesium, calcium, strontium, and aluminum are suitable for this purpose and are in some respects more desirable since they can tolerate a somewhat higher moisture content than the mixtures with unreacted CrO_3, and can in fact be mixed in atmospheres having a humidity of as much as 75% or more. It appears that these dichromates are less hygroscopic than CrO_3, and not only is less precaution needed for the mixing, but the mixture need not be so carefully sealed.

The reducing agents can also be partially or completely protected from contact with the CrO_3 or the dichromate. One simple way to do this is to introduce the ingredients into a container in such a manner that they do not mix to any appreciable degree. There will then be a fairly thin boundary layer between the ingredients where the only actual contact of the reactants will occur. The reducing agent particles can also be first thoroughly mixed with very fine powdery forms of the above zinc, magnesium or aluminum oxides, so that the particles tend to become coated by these oxide powders and thereby somewhat insulated from the CrO_3.

As described in applications Ser. Nos. 708,772 and 738,648, as well as Ser. No. 666,852 filed June 20, 1957, Ser. No. 708,772 filed Jan. 14, 1958, and Ser. No. 814,200 filed May 19, 1959, now Patent 3,053,702, the coatings of the present invention can also contain hydrophobic resins and/or pigment. These ingredients are provided in a form in which they are dispersed in water so that they readily mix with additional water to form the final coating solution. Concentrated resin dispersions having as much as 50% resin solids by weight are available, and in those concentrated dispersions the reducing agent of the present invention can be dissolved to form a stable concentrate which has compactness features approaching those of pastes. Such a formulation can be readily dissolved in water to the required dilution, and then mixed with the necessary solution of CrO_3 or dichromate to form a coating solution that applies a resin containing coating as described in the last mentioned prior application. An illustration of such a concentrate is as follows:

EXAMPLE II

One gallon of an aqueous hydrophobic resin dispersion made as described below and containing 46% of solids by weight.

One gallon of a 50% by weight solution of sucrose.

The two liquids are mixed and yield a viscous stable milky dispersion that can be kept indefinitely and will, after dilution to 4% solids weight and in combination with an equal volume of a 6% CrO_3 solution in water added in the form of $ZnCr_2O_7$, provide a coating bath that when applied with rubber-covered rolls gives a very effective coating on AISI types 400 and 300 stainless steel, aluminum, and galvanized steel, with a 5 second cure at 400° F.

The above resin dispersion is made by mixing:

3300 milliliters of deionized water,
200 grams of para-normal octyl phenoxy octaethoxy ethanol,
1000 grams of inhibitor-free methyl methacrylate,
800 grams of inhibitor-free ethyl acrylate,
36 milliliters of a solution of 0.3 gram $FeSO_4 \cdot 7H_2O$ (reagent grade) in 200 milliliters deionized water,
9 grams ammonium persulfate.

This mixture at room temperature is placed in a glass container and stirred while there is added

9 grams sodium metabisulfite,
2.5 grams t-butyl hydroperoxide.

Stirring is continued until the temperature subsides after an initial rapid heat evolution. The reaction mixture is then cooled to room temperature and to it is added another batch of the same ingredients, all but the t-butyl hydroperoxide being dissolved in a quantity of deionized water ¼ of that used in the original batch. The t-butyl hydroperoxide is then added with stirring to cause the second batch to react and bring the resin content to about 46%.

Other resins such as methyl methacrylate homopolymers, the alkyds, butadiene-styrene copolymers, polystirene, polyvinyl chloride and even polytetrafluorethylene, can be used in place of the resin of Example II with similar results. In general the proportion of resin to reducing agent should be between about 1:2 and 6:1 by weight, and the concentrates have at least about 30% nonvolatile ingredients (essentially resin plus reducing agent) by weight. Specific examples of using such other resins are given in applications Ser. No. 708,772, Ser. No. 738,648 and Ser. No. 814,200.

The degree of corrosion resistance imparted by the resin-cotaining coatings whether the resins are waxy or non-waxy, is so high that additional protective films are not needed. Hydrophilic resins, such as polyacrylic acid can also be used.

Pigments can also be incroporated in the above concentrated resin dispersions, or where resin-free mixtures are desired, the reducing agents can be incorporate in the pigment dispersions of the type referred to for instance in application Ser. No. 814,200. Effective examples of such concentrates are:

EXAMPLE III

50 cc. of a 50% by weight solution of sucrose in water, 285 cc. of an acrylate resin prepared as described in

Example II but with a ratio of methyl methacrylate to ethyl acrylate of 1:4 by weight,

167 cc. of an aqueous dispersion of a mixture of 95% carbon black and 5% phthalocyanine blue, the dispersion having a 25% solids content and stabilized with para-normal octyl phenoxy triethoxy ethanol in a concentration of 0.05%.

The three ingredients are mixed together to form a stable dispersion that will keep without any of the ingredients settling out. Before use it can be first mixed with 100 cc. of an aqueous solution of zinc dichromate having a concentration of 1.05 grams zinc dichromate per cc. and then diluted to 1 liter with water. The resulting mixture forms a very effective black coating on bare steel either plain or pre-etched with nitric acid, if the mixture is rolled onto the steel with rubber rolls and the thus coated steel heated with a gas flame to 400° F. for one and one-half seconds.

EXAMPLE IV

300 cc. of the acrylate resin dispersion similar to that of Example II, sold by Rohm & Haas, Philadelphia, Pennsylvania, under its designation Rhoplex C–72,

30 cc. of an aqueous solution of para-normal octyl phenoxy tetra-ethyl ethanol having a concentration of 20% by weight,

100 cc. of a 50% by weight aqueous solution of sucrose,

200 cc. of an aqueous dispersion of phthalocyanine blue containing 25.6% pigment by weight and stabilized with 0.1% of the above para-normal octyl phenoxy tetra-ethoxy ethanol,

54 cc. of an aqueous dispersion of titanium dioxide containing 36% TiO_2 by weight and 3.3% hydroxy ethyl cellulose.

The resulting mixture can be stored for indefinite periods although after some time some of the titanium dioxide will settle out. The settled material redisperses itself readily upon stirring.

Before coating there can be added to the mixture 300 cc. of an aqueous solution of zinc dichromate having 0.7 gram of the dichromate per milliliter, and it is then ready for application by a conventional spray gun. Aluminum construction panels so sprayed and then cured by holding for ten seconds in an air oven kept at 1000° F., show better outdoor resistance than anodized colored aluminum.

Straight chromium steel, stainless steel, aluminized steel, galvanized steel and bare steel panels similarly coated are very satisfactory surface panels for building construction. Other pigments such as iron oxide reds, chrome yellows and chrome oxide pigments and the like, also can be used in place of the pigments of the above examples, or can be combined with other pigments to give varying colors.

Some reducing agents such as those which are ionizable salts, tend to render dispersions unstable and are better avoided in the making of concentrated resin- and/or pigment-containing dispersions. The nonionic polyalcohols such as sucrose, glycerine and the like do not show this destabilizing tendency.

The wetting agents used in the above examples are very effective in keeping the resin and/or pigment particles dispersed, but they can be replaced by other nonionic, anionic or cationic wetting or suspending agents without affecting the corrosion resistance of the final coating.

Anhydrous coating mixtures of a hexavalent chromium compound with a reducing agent can also be prepared in relatively stable form with such reducing agents as polyethylene glycols having molecular weights of at least about 4000. These glycols are unctuous or waxy in nature and accordingly are much more intimately in contact with the hexavalent chromium compound with which it can be uniformly or nonuniformly mixed. While this intimate contact generally makes for a poor stability, these glycols are so resistant to oxidation at temperatures as high as 225° F., that the mixtures can be stored for many months at 180° F. without loss of usefulness.

One example of such a long-lived mixture is prepared by mulling 3.5 parts by weight of zinc dichromate powder with 1 part by weight of polyethylene glycol having a molecular weight of 8,000. CrO_3 can also be used in place of the zinc dichromate.

The proportion of chromium that is reduced to trivalent form in the coating of the present invention is preferably at least 70% of the total chromium present. Lower conversions leave the final coating with a brownish appearance and also do not give the best corrosion resistance. When the reducing agent is decreased in amount so that the chromium conversion drops below 40%, the curing time is increased and begins to become a serious obstacle. For instance, the complete elimination of a reducing agent from the resin-dichromate coating formulations produces coatings that are sensitive to moisture and do not provide sufficient protection unless the curing is carried out for at least five minutes at a minimum temperature of 350° F. Even then the chromium conversion is about 30% with a resin-to-dichromate ratio of about 2:1 only the CrO_3 content of the dichromate being considered, and the conversion is even less with lower proportions of resins.

Such inadequately converted coatings are greatly improved by a hot water wash, apparently because some unconverted material is dissolved out. For instance, a product coated as in the above Example IV and cured for ten minutes at 325° F., develops better corrosion resistance and a more brilliant color if washed for one minute with 180° F. tap water. After such washing the chromium conversion analyzes at about 58%. For this improvement the washings should bring the conversion to at least 50% and generally at least a one-half minute treatment with water 160° F. or hotter is needed. The same improvement is brought about with all the resins and pigments and in coatings containing neither.

The coating formulations of the present invention are especially effective when the hexavalent chromium is in the form of zinc dichromate. This dichromate is inexpensive as well as very soluble in water and at the same time it shows an exceedingly low tendency to oxidize reducing agents when in water solution. It is accordingly the preferred form of hexavalent chromium.

The protective nature of the above coatings, whether or not containing resin, is also of value in extending the life of scalpels, razor blades, and the like. By way of illustration, a scalpel made of plain carbon razor steel when carrying a resin-free cured coating deposited from a solution of 1% chromic acid and ⅓% sugar, can be used for as many as five separate operations before it need be discarded. A similar razor blade also has a two to fourfold increase in life when used for normal shaving. Such results are also obtained when the coating is deposited from a solution that, in addition to the chromic acid, contains resin in the proportions of the present invention, and the resins can be either thermoplastic or thermosetting. It appears that the life of a razor edge is determined to a large extent by corrosion, particularly where the edge is only used during widely spaced intervals of time.

Aluminum-surfaced and stainless steel building panels, storm windows, etc., that are exposed to weather are also very desirably coated in the above manner. The coatings greatly reduce pitting and corrosion whether or not the resin is included with the chromic acid or dichromate, and whether the resin is thermoplastic or thermosetting.

It is a feature of the above-described resin-free coatings of in situ formed mixed chromium oxides, that they behave as though they are electrically conductive. One example of such behavior is that electroplatings can be applied over the coatings. Chromium, for instance, can be readily deposited at room temperature from an aqueous

solution of 400 grams of chromic acid and 4 grams H_2SO_4 per liter, the coated metal being connected as a cathode, and using a cathode current density of 50 amperes per square foot. The current density can range from 20 to 100 amperes per square foot, and the temperature can range from about 60 to 140° F. The chromium deposits as a dull layer that adheres to the oxide coating, but can be removed by electrolytic stripping, using the chromium plating as an anode in an aqueous solution of 5% sodium hydroxide. After stripping, the mixed chromium oxide coating of the present invention is found still adhering to the base metal.

Copper, nickel, zinc and the other metals can also be electroplated over the coating of the present invention, in place of or in addition to the chromium, and any or all of these metals can be so plated on the mixed chromium oxide coating regardless of the base metal which carries the coating.

In the coating of continuous sheets the use of liquid quenching is desirable apart from the improved corrosion resistance it contributes. When a coil of such sheet emerges from the curing oven of a coating sequence, the metal might not cool rapidly enough to permit immediate recoiling. Such recoiling is best carried out with the metal no hotter than about 175° F. Liquid quenching will then immediately bring the metal down to recoiling temperature. Water-cooled rolls can also be used to cool down the metal, and forced air drafts are likewise helpful, but they do not contribute the extra corrosion resistance, and do not supply the small amount of free chromic acid that can be conveniently added to a quenching liquid.

The use of a quenching liquid also provides a simple way to increase the conversion ratio of the chromium in the coating, as described above. For example, in an extreme situation where as originally cured the conversion is only 20%, a half-minute wash with 165° F. water will increase the conversion to 40%. Hotter water will increase the conversion in shorter times.

To illustrate the long life of polyethylene glycol coating formulations, a polyethylene glycol having a molecular weight of about 9000 can be dissolved with about six times its weight of zinc dichromate in water to form a solution having 3% of equivalent CrO_3 content, and this solution even after a continuous boiling for eight hours will show no sign of any precipitation. Upon curing at 280 to 500° F., however, films of these polyethylene glycols will reduce the hexavalent chromium of the coating in a matter of only one to three seconds. Polyglycols having as many as 400 glycol units can be used and will even show greater stability under boiling conditions without materially prolonging the curing time. On the other hand, the stability begins to taper off substantially as the number of glycol units is reduced below 40. A polyethylene glycol having a molecular weight of 300 will for example become useless after boiling for only about one hour in an aqueous solution that also contains zinc dichromate. Smaller molecular weights show even greater instability.

Dry mixtures of zinc dichromate and these polyglycols are more stable than their aqueous solutions. Inasmuch as temperatures of about 120° F. are about the maximum normally encountered in commercial shipping and storage operations, the particularly desirable mixtures have polyglycols that melt at temperatures above 120° F. In the case of polyethylene glycol, this calls for a molecular weight of at least about 3000.

In addition to polyethylene glycol, polypropylene glycol and polytrimethylene glycol show the same high stability as well as effective reducing power upon curing. Compounds that include the polyethylene glycol structure, such as the alkaryl polyethoxy ethanol type wetting agents, also behave similarly.

At temperatures of about 150° F. and higher, zinc dichromate shows a strong tendency to hydrolyze in aqueous solution and deposit some insoluble normal zinc chromate. To avoid filtering off such a deposit there can be added to the hot bath just enough chromic acid to prevent the hydrolysis. About 5% of free chromic acid, based on the total weight of the zinc dichromate, is generally adequate for this purpose and the resulting mixture shows the remarkable stability described above notwithstanding the presence of this free acid.

Although the polyglycols having less than 40 glycol units per molecule are not too satisfactory for very high temperature coating baths, they do help materially in extending the useful life of cooler coating baths such as those used at room temperature. A polyethyleneglycol having a molecular weight of only about 200 (tetraethyleneglycol) will by way of example show in a 10% aqueous solution of zinc dichromate at room temperature, a useful life of as much as a month or more, and such a life cannot be obtained with reducing agents like sugar. This increase in low temperature stability is of particular value when the coating formulation also contains other ingredients suspended or dispersed therein. Thus resin-containing coating formulations as described in U.S. Patents 3,053,693 and 3,053,702, such as one in which a polymethyl-methacrylate dispersion is mixed with an aqueous solution of zinc dichromate to form a coating composition having 5% resin and 6.5% of the dichromate, will remain free of flocculation or precipitation for a much longer period of time when these polyglycols are used as the sole reducing agent. All the other resin and pigment-containing formulations of those patents are similarly rendered more stable. For such resin-containing formulations it is preferred to have a polyglycol compound with not over about ten glycol units per molecule. Polyglycols with a greater number of glycol units tend to render the final cured coating somewhat cloudy and inferior.

This aspect of the invention is illustrated by:

EXAMPLE V

548 grams of 1:1 methyl methacrylate-ethyl acrylate copolymer in the form of an aqueous emulsion containing 40% polymer solids
7.6 grams of p-octyl phenoxy dodecaethoxy-ethanol
99.6 grams heptaethylene glycol
128 grams TiO_2
41 grams phthalocyanine blue
11 grams Cellosolve (hydroxyethyl cellulose) to help disperse the pigments
418 grams zinc dichromate
water to make one gallon

This formulation produces a very bright blue coating when applied with a roller and cured. The color is brighter than is obtainable with sucrose substituted for the heptaethylene glycol.

Another feature of the above polyglycol combination is that these polyglycols are more effective than sugar in securing the desired conversion of hexavalent chromium to trivalent condition. Whereas it is generally preferred to use sugar in an amount one-third that of the CrO_3 present in the zinc dichromate in order to obtain a conversion of about 90 to 95%, the polyglycols effect the same degree of conversion when used in a proportion of about 22 to 25% by weight of the equivalent CrO_3 content. In other words, only about three-fourths as much polyglycol is needed as sugar. However for curing operations carried out in five seconds or less it is preferable to have the polyglycol used in the same amount as sugar would be used. Smaller degrees of conversion likewise take smaller amounts of the polyglycols.

The above stability effects of polyglycols for hot zinc dichromate solutions are obtained to a lesser degree with hot chromic acid solutions.

Water-soluble dichromates of other metals that have a valence greater than one will show the same more stable properties described above for zinc dichromate. Desirable examples of such other metals are magnesium, calcium, barium, strontium, aluminum, and nickel.

The coating resins can be the usual thermoplastic acrylates such as mixtures of methyl methacrylate and ethyl acrylate, as described in U.S. Patent 3,053,702, or they can be butadiene-styrene copolymers particularly of the thermosetting kind, or any other coating resin including thermosetting acrylics. Typical resins of this type are described in the June 1961 issue of Industrial and Engineering Chemistry, pages 458–468, and they can be emulsified in water either as toluene or xylene solutions, or as polymers that have been freed of all organic solvents or that were emulsion polymerized initially. These thermosetting acrylic resins are polymers that contain the acrylamide or acrylic acid or hydroxy alkyl acrylate structure and are cross-linked by baking at 300° F. or thereabouts in admixture with cross-linking agents such as formaldehyde, di- or poly-epoxy compounds, or amino resins.

When the above thermosetting acrylic resins are used in admixture with CrO_3 or a water-soluble dichromate of a metal such as zinc that has a valence greater than one, the resin cure is shortened from the usual thirty minute period to less than five seconds.

The final coatings so produced have about 95% of the chromium is trivalent condition.

Even in the absence of reducing agent, the cure shortening described above takes place, although the coating so produced is not as desirable as those produced within the above ranges of chromium conversion.

The coatings of the present invention are extremely effective for protecting readily corrodible metals such as plain carbon steel. Articles such as steel wool can also be protected against premature corrosion by the chromium-containing coatings that are free of resin or that contain resin, but the curing of such coatings on steel wool should be carried out carefully at a relatively low temperature or in an inert atmosphere to keep the steel wool from igniting.

The resin-free or resin-containing coatings of the present invention are also highly suited to protect other metals. Aluminum bases for incandescent lamps are effectively protected by the resin-free coatings that weigh about 10 milligrams or less per square foot. The use of such thin coatings permits leads to be soldered directly to the coated metal, using aluminum solder, without having to remove the coating from the solder site. Such lamp bases can be unanodized or anodized, and the coatings stand up under the high temperatures the bases are subjected to during use.

Black coatings of the above type radiate heat in a very effective manner. Such coatings made with a mixture of carbon black and phthalocyanine blue to provide the black color, give closely reproducible radiation characteristics and are particularly desirable for this reason. TiO_2 can also be added in an amount up to about 50% of the carbon black to further improve the results. Coatings containing appreciable amounts of TiO_2 have very good resistance to the transfer of heat and this resistance is further improved by a superficial stratum of aluminum as in Ser. No. 222,864. The thermoplastic resins such as thermoplastic acrylates, become thermosetting during the curing step by reason of the action of the hexavalent chromium, and can be used to good advantage to make the above black or TiO_2-containing coatings.

Because of this and their chemical inertness, the mixed chromium oxide coatings of the present invention are also suitable for applications to rockets, satellites and the like, as well as to highway signs, such as those made of aluminum.

The pigment-containing mixed chromium oxide coatings of the present invention, with or without the resin, also make very durable coloring surface layers for asbestos panels, tiles and shingles such as those used as walls and siding in building construction. The unusually high alkaline resistance of these coatings gives them an unusually long life on these materials which are usually made from asbestos and portland cement. Such panels can be painted with these coatings to give them a permanent surface layer that, if desired, can change their color. Such coatings can be applied during manufacture, or after the walls or siding have been in use. The curing of the coating to convert 40 to 95% of the chromium to the trivalent condition is readily accomplished on finished walls and sliding by a blowtorch, inasmuch as the panels keep the inner portions of the wall from being affected by the short heat treatment that is required. The conversion changes the appearance of the coating so that it is readily followed by the eye, and unintentional repeated heating of any area is thus avoided.

Zinc surfaces seem to be chemically attacked slowly by hot aqueous solution containing chromic acid and polyethylene glycols that are relatively resistant to chromic acid, that is have molecular weights of at least about 3000. At temperautres above 160° F. the contacting of such solution in which the chromic acid content is at least about 1%, for about 2 to 10 seconds with zinc surfaces give a more corrosion resistant coated cured product than one formed the same way but with a 140° F. contacting temperature.

The wetting agents used in hot coating baths according to the present invention are preferably of the type that have very long polyethoxy chains, as in the p-octyl phenoxy tetracontaethoxy ethanol of the foregoing example. A chain of at least about 30 ethoxy groups along with the phenoxy attachment, provides sufficient resistance to the hexavalent chromium to keep such a wetting agent from premature destruction. This is particularly helpful in coating formulations that have dispersed resin and/or pigment that tend to flocculate out unless dispersing agents are present in significant concentration.

The use of hot coating formulations is desirable particularly in dip type coating techniques because they deposit hot coating layers which tend to dry promptly upon removal of the coated substrate from the coating station. This reduces somewhat the amount of concentrated heat needed for the coating, and also leaves the dried uncured coating less vulnerable to disturbances that would mar a liquid film.

The coatings of mixed chromium oxides including hexavalent chromium, when containing not more than three parts resin for every one part of free or combined CrO_3, can be abraded to give different surface effects without becoming gummy. With or without the resin they make very effective corrosion protection for steel typewriter and adding machine parts, magnesium surfaces of tape recorder reels, zinc base die castings such as pressure cooker weights that are exposed to high temperatures, and other such severely treated materials. Such coatings also withstand cold working of the metal to which they are applied, particularly if the metal has a zinc surface. Steel wire so coated can be drawn to a smaller size. For heavier coatings on every thin wires, e.g. those ½ mil thick, it is better to include in the coating at least about 20% TiO_2 by weight inasmuch as the coating dispersion otherwise tends to run off and leave relatively thin layers.

The mixed chromium oxide coatings of the present invention can also be applied from coating dispersions that are thickened as by the addition of 1–5% silica gel, or by adding other pigments in gel form. Hydroxyethyl cellulose, carboxymethyl cellulose and other thickeners are also suitable. The coating formulation of Example X in Ser. No. 222,864 has 0.23% hydroxyethyl cellulose, but for heavier coatings its concentration can be increased to 0.43% to keep such heavier coatings from draining or running. Higher concentrations cause the final product to have a dull appearance.

The resin-containing mixed chromium oxide coatings can also be used to insulate the laminations of transformer cores or the like, since they can be deposited in very thin films having good electrical resistance as well as high temperature life. From about ½ to 3 parts resin by weight should be used for every part of free or combined CrO_3

in such a coating, and thermoplastic acrylate resins are preferred for this purpose.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. An asbestos cement panel coated with a thermosetting hydrophobic layer of a protective resin and in situ formed mixed hydrated chromium oxides, 40 to 95% of the chromium in the chromium oxides being trivalent, the remainder hexavalent, and resin-to-chromium oxide proportion being from about 5:1 to 1:5 by weight.

2. An asbestos cement panel according to claim 1 in which the coating also contains pigment, and at least 70% of the chromium is in trivalent condition.

3. An asbestos-cement panel coated with a protective pigment-containing layer of in situ formed mixed hydrated chromium oxides, 40 to 95% of the chromium in the chromium oxides being trivalent, the remainder being hexavalent.

References Cited

UNITED STATES PATENTS

2,114,692	4/1938	Ward.	
2,372,284	3/1945	Marc	117—126
3,011,988	12/1961	Luedke et al.	117—126 X
3,094,435	6/1963	Schuster et al.	148—6.2 X
3,128,546	4/1964	Schuster et al.	29—495
3,318,716	5/1967	Schuster et al.	148—6.2 X
3,346,522	10/1967	Schuster et al.	148—6.2 X

FOREIGN PATENTS

759,801	10/1956	Great Britain.

RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

117—132, 161; 148—6.2; 260—29.6