

1

3,177,085

SILICA SOL-MASKING IN GALVANIZING PROCESS

Nicholas M. Adams, Chicago, Ill., assignor to Nalco Chemical Company, Chicago, Ill., a corporation of Delaware

No Drawing. Filed July 27, 1960, Ser. No. 45,545

4 Claims. (Cl. 117-5.5)

The present invention relates to an improved method for galvanizing ferrous metals. Specifically, the invention relates to an improved system for single side galvanizing of various types of ferrous metals.

Galvanizing is a well known method for coating the surfaces of ferrous metals to improve their ability to withstand various types of corrosion. In addition to improving the corrosion resistance of ferrous metals, galvanizing quite frequently improves the outer appearance of the metal piece so coated. While galvanizing is acceptable for forming protective coatings on a large number of ferrous metal parts, in some applications, the surface formed by the galvanizing operation is undesirable. This is particularly true where it is necessary to weld pieces of metal together since it has been experienced that the zinc film on ferrous metals will tend to form a harmful coating around the electrodes when resistance welding techniques are employed.

In the production of automobile bodies, it is desirable that certain surfaces be protected by galvanizing while, in other instances, it is beneficial that a metal surface does not have a galvanized coating, thereby rendering resistance welding and surface finishing operations, such as painting or lacquering, more simple to perform.

To overcome the difficulties experienced where it is sought to protect only a portion of a metal surface with a galvanized coating, there has arisen a process which is generally known to the art as "single side galvanizing."

When it is desired to prevent galvanizing from adhering to certain surfaces on a ferrous metal part that is to be galvanized, it has been found that such surfaces may be treated with certain chemicals which prevent the adherence of the galvanized coating thereto. When the metal part is dipped into the hot galvanizing bath of molten zinc, these chemicals tend to form a protective barrier which effectively acts to prevent the zinc from adhering to the coated portion.

Several advances have been made in the art of single side galvanizing with respect to the chemicals employed. Use has been made of alkali metal aluminates, particularly sodium aluminate, and sodium meta silicate for such purposes. While these have proven satisfactory in many respects, in the single side galvanizing of sheet steel, it has been the experience of the art that such materials have a serious disadvantage, since they are oftentimes difficult to remove. This problem is attributed to the fact that these chemicals must be applied as thick coatings in order to be operative.

In order that the zinc galvanized coatings properly adhere to ferrous metal parts, it is essential that the part be completely free of dirt, oils, iron salts, and other undesirable impurities. In order to prepare metal surfaces for galvanizing there are now in use two basic type systems for preparing the metal surfaces prior to the actual galvanizing. In the first system, it is customary to clean the surface after cold rolling using conventional chemical cleaning operations such as vapor degreasing, chlorinated solvent degreasing, or hot alkaline aqueous degreasing type solutions.

The other system used for cleaning ferrous metal surfaces prior to galvanizing is to subject the metal parts to elevated temperatures, under oxidizing conditions wherein

2

all surface residue from cold rolling operations is removed by combustion. The heating step forms oxides on the surface of the metal which are then removed in the second step of the operation which consists in placing the metal parts in a second furnace at annealing temperatures which are at least 1250° F., with the interior of the furnace being blanketed by a reducing gas. After this, the ferrous metal surface is acid pickled, rinsed and air dried.

An object of this invention is to provide an improved method for treating only a portion or one side of a ferrous metal surface to prevent the adherence thereto of zinc in the hot dip galvanizing of such surfaces. Another object is to provide a coating which may be readily removed, after galvanizing.

A further object is to provide a thin coating which may be economically applied to the surface of the ferrous metal prior to galvanizing, whereby such surfaces tend to be non-adherent to hot zinc coatings. Other objects will appear hereinafter.

In accordance with this invention, it has been found that it is possible to selectively galvanize surfaces of metal parts without galvanizing other surfaces by placing upon the surfaces not desired to be galvanized, a coating of colloidal silica, and then galvanizing the parts so treated. The colloidal silicas used in the practice of the invention are preferably colloidal silica sols which have as a continuous phase, a liquid; and as a dispersed phase, a finely divided amorphous silica which has an average particle size of less than one micron and usually less than 150 millimicrons.

In a preferred practice of the invention, the colloidal silica applied to the surfaces of the metal parts not to be galvanized, are aqueous colloidal silica sols. Colloidal silica sols were well known materials and are commercially available from several sources of supply. A typical group of commercially available silica sols that may be used in the practices of the invention are those silica sols sold under the trade name, Nalcoag. Typical sols of this type are presented below in Table I.

TABLE I

Silica Sol	I	II	III	IV	V
Percent colloidal silica as SiO ₂ -----	15	30	35-36	21-22	49-50
pH-----	8.6	10.2	8.6	3.7	9.0
Viscosity at 77° F., cps-----	Less than 5	Less than 5	Less than 5	Less than 10	20-30
Specific gravity at 68° F-----	1.00	1.205	1.255	1.06	1.385
Average surface area m. ² per gram of SiO ₂ -----	330-430	190-270	135-190	135-190	120-150
Average particle size millimicrons-----	7-9	11-16	16-22	16-22	20-25
Density, #/gallon at 68° F-----	9.1	10.0	10.5	8.8	11.6
Freezing point, °F-----	32	32	32	-10	32
Na ₂ O, percent-----	0.04	0.40	0.10	0.05	0.30

Other silica sols that may be used in addition to those mentioned above may be prepared by using several well known conventional techniques. Perhaps the most convenient method of making aqueous colloidal silica sols is described in Bird, U.S. 2,244,325, wherein a dilute solution of an alkali metal silicate is passed in contact with a cation exchange resin in the hydrogen form whereby the silicate is converted to a dilute aqueous colloidal silica sol. Silica sols of the type described by Bird as produced are relatively dilute. They may be concentrated to more usable concentrations from the standpoint of shipping and application, by employing the techniques described in either Bechtold et al., U.S. 2,574,902; Bragg et al., U.S. 2,680,721; or Parma et al., U.S. 2,601,235. Another

type of silica sol which may be used in the practice of the invention is described in the specification of Reuter, U.S. 2,856,302.

While aqueous colloidal silica sols are preferred for reasons which will be more fully explained hereinafter, it will be understood that other forms of colloidal silica may be employed, such as for instance, sols which contain a major portion of hydrocarbon liquids. Such sols may be generically referred to as organo-sols and are typified by sols of the type described in Marshall, U.S. Patent No. 2,386,247.

In addition to using colloidal silica sols of the types described, it is also possible to use colloidal silica sols which are prepared by dispersing or suspending various types of finely divided amorphous silica powders into various types of liquid media, e.g., water, polar organic solvents, or non-polar organic solvents. Examples of such dispersions of finely divided silica materials are described in the specification of Nohejl, U.S. 2,787,967.

A further highly practical variant of the above described silica sols is prepared by the addition thereto of appropriate thickening agents which are useful in formulating a sol with viscosity specifications calculated for efficient use with any given particular spray or roller coating system. Typical thickeners which have been added to silica sols for this purpose are carboxymethylcellulose compounds prepared in granular powder form from the product of the substitution reaction of an alkali-treated cellulose with sodium monochloroacetate. By this process, a variety of cellulosic compounds can be prepared, having physical characteristics determined by the chain length of the original cellulose starting material, as well as the degree of substitution during the above outlined reaction. Additional choice of thickeners may be made from among methylcellulose compounds having varying chain lengths and degrees of substitution. The invention includes, however, the use of any other commercially available thickeners known to be useful in aqueous and/or non-aqueous systems.

Since galvanizing is a relatively inexpensive method of protecting various types of ferrous metals against corrosion as well as to improve their appearance, it is important that any chemical additive used for purposes of preventing such coatings from adhering to certain portions of the metals treated, does not materially add to the cost of such operations. The colloidal silicas described above, particularly the aqueous colloidal silica sols, in addition to being commercially available, are relatively inexpensive. When used in treating surfaces to prevent the adherence of zinc coatings, it has been discovered that the aqueous colloidal silica sols, as well as other finely divided colloidal silica materials may be used at relatively low concentrations with excellent results being achieved.

In most instances it is expensive to apply the finely divided colloidal silica from a liquid media by either coating or spraying. In the case of aqueous media, it has been found that these materials may be diluted with water to produce concentrations containing as little as 1% by weight of silica expressed as SiO_2 . As a general rule, however, it has been found that the concentration of the silica sols and colloidal silica materials when applied as a liquid can be maintained within the range of from about 1% to 30% by weight with the best results being at higher concentrations to obtain high density films.

The colloidal silicas of the invention are relatively free of alkali metal oxides and have large specific surface areas. As a general rule, the SiO_2 to Na_2O ratio will vary from as little as 10:1 to between 500:1. In some instances, where the silica sols have been deionized, it is possible for these colloidal silica materials to be completely free from metal ions. Similarly the surface areas while capable of variations between 25 sq. meters per gram to about 1000 sq. meters per gram, usually have surface areas within the range of about 25 sq. meters per gram to 400 sq. meters per gram.

In using the aqueous colloidal silica sols of the invention, improved adhesion to the metal surface is obtained by adjusting the pH on the acid side between 3-6 and using certain wetting agents to produce film uniformity. It is desirable that the films of colloidal silica be dried prior to the galvanizing operation. The drying operation may be conducted over various periods of time and at a variety of temperatures. When the treated parts are subjected to continuous high speed galvanizing operations, relatively elevated temperatures, e.g. in excess of 225°F ., are beneficially employed to remove substantially all the water from the aqueous silica sols in order to provide a tenacious thin film of colloidal silica on the surface of the metal prior to annealing and galvanizing.

It is sometimes desirable to remove any silica that might remain on the surfaces after the piece has been galvanized. Removal may be accomplished by standard polishing methods.

Example I

In this example, the test situs comprised a large galvanizing line located in a steel mill. The metal was cleaned prior to the galvanizing step. This particular mill subjected the stack to an annealing process prior to galvanizing. Before annealing, there was installed an oven which heated the surface temperature of the metal up to about 350°F . Prior to the steel coil being drawn through the oven, a bath was installed which contained a dilute solution of the aqueous colloidal silica sol, corresponding to II, Table I. The sol had been diluted with tap water to produce a finished silica concentration of 15% by weight and was adjusted to a pH of 3.5 with a wetting agent added at a concentration of 0.5%. Positioned directly above the bath was a moving roll which picked up the colloidal silica and deposited it on the top side of the surface of the steel coil. The steel coil was then passed through the drying oven and then annealed and galvanized in a standard manner. The zinc coating did not adhere to the side on which the silica coating was applied.

An important advantage of the fine silica coatings of the invention is that even though they are subjected to relatively high temperatures in both the drying and galvanizing operations, they are substantially free from metal ions which, in some instances, will tend to react with the metal surface thereby interfering with its surface properties and characteristics.

It is believed that one of the reasons why the colloidal silica sols described are so effective in preventing galvanized coatings from adhering to the surfaces of the metal treated therewith, is that they tend to distribute very fine particles of colloidal silica uniformly over the surface of the metal. This distribution of extremely fine, submicroscopic particles not only tends to prevent the adherence of the zinc coating to the treated surface, but also tends to improve the surface characteristics of the metal treated.

While the various forms of colloidal silica are easily applied to metal surfaces for the purposes of preventing the adherence of galvanizing thereto, it has been found that the surfaces may be more readily wet by the various colloidal silicas, particularly the aqueous colloidal silica sols, if they are combined with minor amounts of compatible wetting agents. In treating baths and sprays used to coat the surface of the metal prior to galvanizing, amounts of surface active agents ranging from as little as 0.1 to as much as 2% by weight, may be used to improve the wetting ability of the colloidal silicas. The preferred group of wetting agents are the non-ionic type which are exemplified by octylphenol which has been reacted with nine mols of ethylene oxide. Similarly, the block polymers sold under the trade name of "Pluronic" and which are the subject matter of Lunsted, U.S. Patent No. 2,674,619, are also admirably suited for use in conjunction with colloidal silicas.

The invention is hereby claimed as follows:

1. A method for galvanizing only a portion of a ferrous metal object which comprises the steps of applying to the surfaces of the object not to be galvanized, a coating of an aqueous colloidal silica sol, consisting essentially of silica particles of a size less than 150 millimicrons and in an amount of from 1% to 30% by weight SiO_2 , heating the surface so treated to a temperature sufficient to substantially dry the sol, and form a thin film of colloidal silica, and galvanizing the metal object.

2. A method for galvanizing only a portion of a ferrous metal object which comprises the steps of applying to the surfaces of the object not to be galvanized, a coating of an aqueous colloidal silica sol, consisting essentially of silica particles of a size less than 150 millimicrons and in an amount of from 1% to 30% by weight SiO_2 , heating the surface so treated to a temperature sufficient to substantially dry the sol, and form a thin film of colloidal silica, and galvanizing the metal object, and then removing any excess silica from the non-galvanized surfaces.

3. A method for galvanizing only a portion of a ferrous metal object which comprises the steps of cleaning the surfaces of the metal to remove dirt and oxide coatings therefrom, applying to the surfaces of the object not to be galvanized, a coating of an aqueous colloidal silica sol, consisting essentially of silica particles of a size less than 150 millimicrons and in an amount of from 1% to 30% by weight SiO_2 , heating the surface so treated to a temperature sufficient to substantially dry the sol, and form a thin film of colloidal silica and galvanizing the metal object.

4. A method for galvanizing only a portion of a ferrous metal object which comprises the steps of cleaning the surfaces of the metal to remove dirt and oxide coatings therefrom, applying to the surfaces of the object not to be galvanized, a coating of an aqueous colloidal silica sol, consisting essentially of silica particles of a size less than 150 millimicrons and in an amount of from 1% to 30% by weight SiO_2 , heating the surface so treated to a temperature sufficient to substantially dry the sol, and form a thin film of colloidal silica, and galvanizing the metal object and then removing any excess silica from the non-galvanized surfaces.

References Cited by the Examiner

UNITED STATES PATENTS

1,550,629	8/25	Paulus	117—5.5
1,651,403	12/27	Mougey	29—490
2,197,622	4/40	Sendzmir	117—51
2,498,485	2/50	Clawson	117—5.5
2,507,068	5/50	Underwood	22—192
2,557,983	6/51	Linder	117—5.5
2,559,969	7/51	Kennedy	117—5.5
2,787,968	4/57	Luvisi	117—127
2,894,850	7/59	Greene	117—515
2,932,864	4/60	Mellen et al.	22—192
3,013,898	12/61	Dempey	117—169

RICHARD D. NEVIUS, *Primary Examiner*.

JOSEPH B. SPENCER, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,177,085

April 6, 1965

Nicholas M. Adams

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 30, for "II" read -- III --; line 73, for "Lunsted" read -- Lundsted --; column 6, line 26, for "117-515" read -- 117-5.5 --.

Signed and sealed this 21st day of September 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents