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[54] REGENERATION OF CHROMIC ACID
ETCHING SOLUTIONS

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204/30, 38; 117/47 A; 106/287; 148/6.2

[56] References Cited

UNITED STATES PATENTS

- 2,890,944 6/1959 Hays 156/19

3,317,330 5/1967 Livingston et al. 106/287

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[57] ABSTRACT

A spent chromic acid etching solution, which has been used, for example, to etch plastic substrates, is regenerated by adding, with mixing, an alkali metal permanganate, such as potassium permanganate, and separating the resulting sludge which forms. During the regeneration process trivalent chromium in the etchant is oxidized to hexavalent chromium. The regenerated etching solution, thus recovered, is utilized as an etchant per se or it may be reconstituted with added sulfuric acid and/or chromic acid as required.

6 Claims, No Drawings

REGENERATION OF CHROMIC ACID ETCHING SOLUTIONS

This invention relates to a method for regenerating spent chromic acid etchant solutions. More particularly, this invention relates to a process in which spent or depleted chromic acid etching solutions are regenerated through the addition, with mixing, of an alkali metal permanganate. Another embodiment of this invention relates to a continuous etching process.

The surfaces of certain plastic articles, such as polypropylene plastics, are normally hydrophobic and unresponsive to most lacquers, printing inks, dyes and metals sought to be deposited from solutions of their salts either by electroless plating methods or in vacuum volatilization, etc.

A variety of processes are known in the art for preparing the surfaces of plastic substrates, such as polypropylene, acrylonitrile-butadiene-styrene (ABS), etc., for subsequent metal plating operations, wherein the surface is rendered more receptive to the deposit thereon of a metal plate or film and a firmer bond of the deposited metal to the substrate is produced. It is common knowledge that non-conductors such as plastic, glass and ceramics can be electrolessly plated with metal deposits or metals films if the surface of the substrates are first properly conditioned by chemical or mechanical means. Commonly the surface of certain plastics, such as ABS, polypropylene, polycarbonate plastics, etc., are prepared for electroless plating by chemical means utilizing etching solutions. Chemical etching, as it is commonly referred to, involves a process of deglazing the surface without seriously roughening it, in contrast to the result usually obtained when mechanical processing is employed. A low level degree of roughening is desirable since this facilitates the subsequent production of metal deposits of greater smoothness and brilliance in the finished article.

Chemical etching of plastic substrates is generally well known in the art and many solutions useful for this purpose are described in the literature. In general these prior art solutions consist essentially of a formulation of sulfuric acid together with chromic acid and, in addition, phosphoric acid, if desired. The contacting of the surface of the plastic substrate in the etching operation may be done in any conventional way, as by dipping or spraying and is continued for a period of time sufficient to produce the desired effect.

A number of processes for etching the surface of plastic substrates to make them more receptive to deposition of metals in electroless plating are described in the art. For example, in U.S. Pat. No. 2,886,471 a process is disclosed for treating polyethylene products by the oxidation of the surface of the plastic with a strong sulfuric acid/dichromate solution whereby the surface is readily made hydrophilic and adaptable to electroless plating. The strong sulfuric acid/dichromate solution may be obtained by saturating concentrated sulfuric acid with technical sodium dichromate. The surface is treated by passing the plastic product through a bath of the oxidizing solution and then washing in cold water.

In a process described in U.S. Pat. No. 3,317,330 the normally inert, hydrophobic surface of polypropylene or polyethylene is immersed for a few seconds in a bath containing approximately 90 percent of a strong acid, such as sulfuric, and small amounts each of potassium permanganate, (0.013 percent by weight maximum), water, chromic acid (chromium trioxide) and a perfluoroalkyl-type wetting agent, rinsing the surface with water and then drying it. The bath composition of U.S. Pat. No. 3,317,330 is prepared in the following manner. Sulfuric acid is poured into a lead-lined vessel at standard temperature and pressure. Water is then poured into another container and weighed amounts of chromic acid and potassium permanganate are added to the water to form a homogeneous mixture. The homogeneous solution is then added slowly and with constant mechanical agitation to the tank containing the sulfuric acid and at this time the wetting agent is added to the bath. The function of permanganate in this process is to permit the deposition of an invisible predominately manganous film on the polymer surface thus enhancing the bonding characteristics.

The degree of treatment or modification of the normally hydrophobic surface of the plastic can be regulated by varying the temperature and strength of the etching solution as well as the exposure time of the surface to the solution. With strong solutions at moderate temperatures the surface is rendered hydrophilic in about 0.5 to about 5 minutes. After the treatment, water is found to spread evenly over the plastic surface instead of gathering in drops as in the case with an untreated surface. A preferred etching composition consists of approximately 14 percent by weight of chromium trioxide 40 percent by weight of sulfuric acid (66°Be.) with the balance being water. Usually this solution is employed at approximately 150° F. and the plastic substrate is immersed in or otherwise contacted with it for a period of from about 1 to about 10 minutes or more.

Although the chromic acid-sulfuric acid-water etching solution described above is generally satisfactory for converting the hydrophobic surface of plastic substrates, such as ABS (acrylonitrile-butadiene-styrene), polysulfones, polypropylenes, polystyrenes, epoxys, phenolics, polybenzimidazoles, polyphenylene oxides, acrylics and the like to a receptive hydrophilic surface, a number of problems present themselves in operating such systems commercially. Etching processes, known in the art using such etching solutions, suffer from the following disadvantages:

1. The efficiency of the chromic acid solution drops off rapidly and when treating polypropylene after only about 40 percent of the hexavalent chromium ions are reduced to trivalent chromium ions during the oxidation process, the bath becomes inoperative.
2. The present practice of discarding the spent chromic acid bath and concurrent waste disposal problems are particularly expensive and time consuming.
3. The frequent handling of large quantities of such highly corrosive etching solutions in filling the etchant tanks and discharging the spent solution in a manufacturing process is hazardous to personnel since contact with the skin may result in severe burns.

During the etching process, there is some loss in weight from the surface of the plastic as a result of the oxidation action of the chromic acid etchant. At the same time the hexavalent chromium ions of the chromic acid are reduced to the trivalent form during the oxidation reaction and, consequently, the concentration of the hexavalent ions gradually decreases. Furthermore, it has been found that the trivalent chromium formed inhibits the oxidation action of the etching solution and when treating polypropylene surfaces after about 30 to about 40 percent of the hexavalent chromium ions of the original solution have been reduced to the trivalent form, the etching rate falls to such a low value that it is commercially unacceptable. Heretofore, such depleted etching solutions were disposed of as, for example, by sewerage after appropriate waste disposal treatment.

There is need in the art, therefore, for an efficient process for regenerating spent or depleted chromic acid solutions which have been used, for example, to etch plastic substrates and it is the primary object of this invention to provide such a process.

Another object of this invention is to provide a method for regenerating chromic acid etchant solutions in such a way as to prolong substantially their life.

Another object of this invention is to reduce the time spent by personnel in the hazardous operation of charging and dumping the etchant tanks.

Another object of this invention is to substantially reduce the cost of etching plastic substrates for reception of a metal film by the electroless plating method.

It has been found that chromic etchant solutions which have been used to etch plastic substrates can be regenerated by adding to the spent or partially depleted solutions with mixing, an alkali metal permanganate selected from the group consisting of sodium, potassium and lithium permanganate and mixtures thereof. If desired, the regenerated etching solution can then be reused, as is, after the sludge which forms during the

process has been allowed to settle to the bottom of the etching solution tank. This usually requires from about 6 to about 12 hours or more. Optionally, the clear regenerated etching solution can be recovered by decantation after the settling period. Also, the sludge can be removed from the regenerated solution by centrifugation, filtration or by any other convenient method. It has been found highly desirable to remove the sludge from the regenerated etchant bath since clogging of the air tubes in the etching tank and reduced agitation with concomitant reduction in efficiency and quality may result if this is not done. After regeneration, it may be desirable to adjust the concentration of the chromic acid, sulfuric acid or phosphoric acid and this can be done by adding the required amounts of these ingredients to the regenerated etching solution. Where an excess of water is present in the regenerated solution, it can be removed by evaporation.

Usually the regeneration process of this invention is conducted at temperatures ranging from about 60° F. to about 200° F. and, preferably, from about 130° F. to about 160° F. The quantity of the alkali metal permanganate added may be varied widely and, generally will be about 1.2 to about 1.7 times the stoichiometric requirement for converting all of the trivalent chromium in the etching solution to hexavalent chromium. Usually, the amount of the alkali metal permanganate added will be from about 0.10 to about 5 lbs. per gallon of the spent or depleted etching solution being treated. Although, advantageously, the alkali metal permanganate compound may be added as a finely divided powder, any other convenient form can be utilized. In operating the process of this invention, the preferred alkali metal permanganate is potassium permanganate.

Caution must be observed in adding the alkali metal permanganate which is an extremely active oxidizing agent. It is essential that the addition be made slowly and carefully. During the addition cycle evolved oxygen and/or ozone causes frothing and foaming of the etching solution to take place.

Spent or depleted chromic acid etching solutions which can be regenerated by the process of this invention are solutions resulting from, for example, the etching of plastic substrates with etchants initially containing from about 1 to about 25 percent by weight of chromium trioxide in solution, at least about 30 percent by weight of an acid selected from the group consisting of sulfuric and phosphoric and combinations of the two, with the balance being water. Generally, the etchant solution has the following initial composition:

Ingredient	Percent by Weight
Chromium Trioxide	About 1 to about 25
Sulfuric Acid	About 90 to about 30
Phosphoric Acid	About 70 to about 0
Water	Balance

It is apparent that the action of the alkali metal permanganate in the regeneration process involves more than mere oxidation of trivalent to hexavalent chromium in the etching solution. During the etching process there is a weight loss by the plastic substrate which results from the oxidation of the plastic surface and it is known that decomposition products which result enter and contaminate the etching solution. Such decomposition products also contribute to the reduced efficiency of the etchant as the concentration builds up with use. The exact mechanism by which the etchant solution is regenerated is not completely understood although it is believed that oxygen or ozone developed on reaction of the potassium permanganate with the sulfuric or phosphoric acid not only effectively oxidizes trivalent chromium ions present in the depleted solution to the useful hexavalent chromium ions but, in addition, converts the contaminants in the solution to a form in which they no longer interfere with the etching process. Surprisingly, it has been found that chromic acid etching solutions regenerated by the process of this invention exhibit etching efficiencies equal to that of the original solutions.

In order to prepare certain polymers other than acrylonitrile-butadiene-styrene (ABS) for subsequent metal deposition current practice involves subjecting some plastic substrates to a pretreatment by immersion in an adhesion promoter which is retained in the surface and facilitates subsequent oxidation by the chromic acid. For example, polypropylene, can be advantageously treated by immersing it in a bath containing emulsified linseed oil or turpentine for about 10 minutes at a temperature of about 170° F. as described in Grunwald and D'Ottavio application Ser. No. 654,901, filed Jan. 14, 1967. Spent solutions resulting from the etching of such pretreated substrates can be regenerated by the process of this invention equally as well as spent solutions obtained in etching those plastic substrates which have not been subjected to surface pretreatment operations.

The following examples illustrate various embodiments of this invention and are to be considered not limitative:

EXAMPLE I

A solution having the following initial composition is utilized in etching polypropylene articles at a temperature of about 175° F.:

Ingredient	Percent by Weight
Chromium Trioxide	14
Sulfuric Acid	40
Water	46

Prior to etching, the surface of polypropylene is pretreated by immersion of the articles in a bath containing emulsified turpentine for about 10 minutes at 170° F. After the above-described etching solution is employed to etch about 60 sq. ft. per gallon of the thus-pretreated polypropylene, the rate of etching diminishes to such a low value that it is below a satisfactory rate for commercial operation. The chromium trioxide content of the depleted solution is 8.5 percent. In addition, at the end of the cycle, the adhesion of the metal coating developed by plating the etched polypropylene article is unsatisfactory. To the spent etchant solution, finely divided potassium permanganate is carefully added to the amount of about 1 pound per gallon of solution over a period of 10 minutes, with agitation, and at a temperature of 150° F. During the addition period, considerable foaming and frothing occurs. The thus-treated etching solution is allowed to settle for 12 hours after which a clear, regenerated solution having a chromium trioxide concentration of 12.6 percent is recovered by decantation. This regenerated solution is again utilized in etching polypropylene articles under the same conditions as before and in treating surface area of about 60 sq. ft. per gallon of etching solution the efficiency of the etching process, is equal to that of the original solution.

EXAMPLE II

A solution of the composition set forth below is utilized in etching ABS articles:

Ingredient	Percent by Weight
Chromium Trioxide	1.4
Sulfuric Acid	88.0
Water	Balance

The articles, which are subjected to etching in this example, are not pretreated in any manner. The above-mentioned solution is utilized to etch ABS articles at a temperature of 135° F. by immersion and after about 50 sq. ft. per gallon has been etched, the adhesion between the ABS and the subsequently deposited plated metal decreases to nearly 0 pounds per inch. The chromium trioxide content of the depleted solution is 0.14 percent. Potassium permanganate (about one-fourth inch size) is then added to the depleted etchant solution in amount of about 0.25 pounds per gallon of solution over a period of about 5 minutes with agitation. During the addition process, the temperature of the bath is maintained at about

135° F. Regeneration of the etchant is accompanied by a substantial amount of foaming and frothing. The thus-treated solution is allowed to settle for about 8 hours and the clear regenerated solution having a chromium trioxide concentration of 1.2 percent is recovered by filtration. Etching of the ABS articles is then continued with the regenerated solution and it is found that a surface area of about 50 sq. ft. per gallon can be satisfactorily etched with the regenerated material. Adhesion of plated metal to the etched articles is equal to that obtained with the original solution.

EXAMPLE III

A chromic acid etching solution of the following composition is prepared:

Ingredient	Percent by Weight
Chromium Trioxide	14
Phosphoric Acid	20
Sulfuric Acid	20
Water	46

The described solution is employed in etching ABS articles at a temperature of 150° F. until the chromium trioxide content to the etching solution reaches a value of 10 percent by weight. At this point, the adhesion of the metal coating subsequently plated onto the etched substrate is below the acceptable commercial value.

Regeneration of the depleted solution is accomplished by adding about 0.75 pound of crystalline potassium permanganate to each gallon of the depleted etchant at a temperature of 145° F. over a period of about 10 minutes with agitation yielding a regenerated etching solution having a chromium trioxide content of about 14 percent. The regenerated solution is again employed to etch ABS articles and the adhesion of metal plated on the etched surface is found to be as satisfactory as that resulting when the original solution was employed.

It is not necessary in employing the valuable regeneration process set forth herein to utilize as the starting material a completely depleted or spent etching solution. If desired, an etching solution which has been only partially depleted, for example, one in which only 5 percent or less of the chromium is present as trivalent chromium, can be efficiently regenerated by the process of this invention in a batchwise or continuous manner.

One embodiment of this invention that is contemplated to enable a chromic acid etching solution to be used indefinitely for etching is a continuous etching process utilizing continuous regeneration of the etching solution. This process is conducted by contacting plastic substrates with a chromic acid etching solution containing from about 1 to about 25 percent by weight of chromium trioxide in solution, at least about 30 percent by weight of an acid selected from the group consisting of sulfuric and phosphoric and combinations of the two with the balance being water, at a temperature of about room temperature to about 200° F. for a period of from about 0.5 to about 30 minutes, continuously removing a portion of a partially spent solution from the etching tank, adding with mixing an alkali metal permanganate selected from the group consisting of sodium, potassium and lithium permanganate and mixtures thereof in the amount of from about 0.10 to about 5 pounds per gallon at a temperature of from about 60° to about

200° F., to regenerate the etching solution, separating the sludge which forms during the regeneration operation by any convenient method, such as by decantation after the sludge has been allowed to settle and recycling the thus-regenerated etching solution back to the main body of the etching solution. Simultaneously, sulfuric acid, chromium trioxide, or phosphoric acid may be added continuously, as required, to maintain the desired concentration of these two ingredients. Thus, the main body of the etching solution can be used to etch continuously until foreign impurities build up to such a point that the quality of the etch is affected. A continuous process of this type obviates the necessity for replacing the spent etching solution and for added waste treatment processes to permit disposal of the spent solution. In the continuous process of etching of this invention the contacting of the plastic surface may be done by any conventional method, such as by dipping or spraying.

Recovered sludge, which consists mainly of manganese oxide (MnO and MnO_2) as well as some potassium sulfate, can be washed, dried and sent to an appropriate process for recovery of the manganese oxides.

Substantial cost reduction in the etchant step of plastic substrates can be achieved utilizing the novel process of this invention. Previously in etching plastic substrates, such as polypropylene, chromic acid etching solutions were usually exhausted after treating no more than about 50 sq. ft. per gallon of solution. However, by using the regeneration process of this invention, the etching solution can be utilized to treat a minimum of 300 sq. ft. of polypropylene per gallon.

What is claimed is:

1. A process for continuous etching of plastic substrates which comprises contacting plastic substrates with a chromic acid etching solution containing from about 1 to about 25 percent by weight of chromium trioxide in solution, at least about 30 percent by weight of an acid selected from the group consisting of sulfuric and phosphoric and combinations of the two, with the balance being water, at a temperature of about room temperature to about 200° F. for a period of about 0.5 to about 30 minutes, continuously removing a portion of the etching solution from the main body of the etching solution, adding from about 0.10 to about 5 pounds per gallon of the etching solution of an alkali metal permanganate selected from the group consisting of sodium, potassium and lithium permanganate and mixtures thereof, at a temperature of from about 60° to about 200° F., separating the sludge formed from the regenerated solution, and returning the said portion of the regenerated etchant solution to the main body of the etching solution.

2. The process of claim 1 wherein the said concentration of the regenerated etching solution is adjusted by adding additional quantities of sulfuric acid and chromium trioxide.

3. The process of claim 1 wherein the said regenerated solution is recovered by decantation after the sludge has been allowed to settle.

4. The process of claim 1 wherein the said alkali metal permanganate is potassium permanganate.

5. The process of claim 1 wherein the said plastic substrate is polypropylene.

6. The process of claim 1 wherein the said plastic substrate is ABS.

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