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CHROME PLATING AND ANODIZING STOPOFF COMPOSITION

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This invention relates to improved acid resistant coating compositions and more particularly to an improved form of coating composition suitable for producing a non-conductive masking or stopoff coating which is highly resistant to strong and highly oxidizing acid baths of the type used in chromium plating as well as of the type used in anodizing.

Chromium plating is normally performed in strong chromic acid baths utilizing small amounts of sulphuric acid. More recently, plating baths have been developed which are self regulating and which permit high speed plating, but even these contain highly oxidizing acid concentrations which will attack and decompose many ordinary types of coatings.

Chromium metal, because of its hardness and ease of lubrication has found extensive use in rebuilding worn tools and dies by electrolytic deposition. Where such tools and dies are to be electrolytically built up with thicknesses of what is commonly known as "hard chrome," either with or without a base layer of nickel, it is usually desirable to apply a coating to mask or stop off those areas exposed to the electrolytic bath on which no plating is desired. Such coatings must have properties sufficient to withstand the severe corrosive conditions for long periods of time. According to Faraday's law, the amount of metal deposited at the cathode is a function of the current and the time. Thus, to deposit an appreciable amount of chromium metal, as in rebuilding of worn tools and dies, extended periods, up to as long as 48 hours or more, may be required for the plating operation. A satisfactory stop off coating for chrome plating use must not only withstand this action of the strong oxidizing acids but also the erosion effect of hydrogen bubbling at the cathode for such extended periods.

Numerous acid-resistant coating compositions have been developed, but a great disadvantage of many of these previous coatings is that they are effective in chrome plating baths only for limited periods. Furthermore, many of the coatings produced from such compositions tend to be porous in some areas, and do not completely prevent penetration of the acid bath. Another common disadvantage is their extreme brittleness which is developed under the highly acid conditions of a chrome plating bath. This brittleness often results in flaking off of the coating under the action of hydrogen bubbling at the cathode.

In coatings for use in anodizing baths, as in chrome plating baths, similar problems have been experienced in connection with previous types of stopoff coatings. Certain metals, such as aluminum and magnesium, are anodized to protect their surfaces against corrosion and wear. In the anodizing process the metal parts to be anodized are placed at the anode and their surface is electrolytically coated with a hard porous amorphous oxide film to give it increased corrosion resistance and durability. Generally the same types of acids as in chrome plating are used, for example chromic and sulphuric. However, many other acids such as boric and oxalic acids have also been employed. With any of these types of acids, whenever selective areas are to be anodized, a stop-off or masking coating must be utilized which will withstand the corrosive action of the acids in the bath.

Another type of process in which masking or stopoff coatings find extensive application is in chemical milling or preferential etching. It has recently been found that such chemical milling or preferential etching is far less

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expensive and as accurate as equivalent operations performed on milling machines or grinders. The properties required of a satisfactory stopoff coating composition are similar to those for protection in electrolytic plating, and include ease of application, rapid curing, resistance of the film to attack by the chemical bath, adherence to the surface, and ease of removal.

It is therefore an object of the present invention to provide an organic coating composition which can be cured at room temperature after application by known painting methods, such as spraying, dipping, rolling, brushing, tumbling, etc. which will form a coating resistant to the action of plating bath acids such as chromic and sulphuric, to the action of anodizing baths, and to chemicals used in chemical milling and etching.

Another object of the invention is to provide a method facilitating selective electroplating onto predetermined areas of a surface by providing a stopoff coating film over the portions of the surface which are to remain unplated.

Still another object of this invention is to provide a stabilized coating composition which will withstand lengthy storage in the liquid state without deterioration of the coating composition and without loss of acid-resistant properties in the coatings produced therefrom.

A further object of this invention is the provision of a coating composition which will form an adhering coating readily strippable by contact with active ketone solvents or with vapor degreasers such as trichlorethylene, perchlorethylene, methylene chloride, and the like.

Still another object of this invention is to provide a coating composition which will form a coating highly resistant to the erosion effect of hydrogen developed at the cathode during electroplating processes.

Another object of this invention is to provide a composition which can form a non-conductive coating which will impede the flow of ions onto selected portions of a metal surface to be immersed in an electroplating bath, thus preventing the molecular formation or metal deposition on the coated areas.

Another object of this invention is to provide a coating composition which can be dried at room temperature to develop full chemical resistances, and can also be force dried to volatilize the solvents therein with an equality resistant film being formed by either drying method.

A further object of the invention is to provide a non-conductive and non-porous stopoff coating composition impervious to anodizing baths for selectively anodizing or forming an oxide film on predetermined areas of a surface of anodizable metals, such as aluminum and magnesium.

A still further object of this invention is to provide a non-porous acid-resistant stopoff coating for protection of predetermined areas of metals in selective etching and chemical milling processes.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description.

These objects are accomplished by adding to a vinyl resin composition containing at least in part a vinyl halide resin, a vinyl chloride-acetate copolymer modified with about 1% interpolymers of maleic acid, a chlorinated biphenyl plasticizer, and propylene oxide as a stabilizer. A suitable solvent or diluent is added to produce the desired viscosity, and an inert extender pigment may be added to provide film homogeneity and to reduce porosity.

The higher molecular vinyl chloride-acetate copolymers are commercially available film forming vehicle constituents which form coatings providing excellent chemical resistance to most inorganic mineral acids. However, these resins cannot be used alone to form satisfactory protective coatings because of their inadequacy

adhesion qualities, brittleness and tendency to flaking. Consequently, other ingredients are necessary. Vinyl chloride-acetate copolymers supplied under the trade name of VYNS by Bakelite Corporation, and certain of the Exon resins supplied by Firestone Tire and Rubber Company have been found to be suitable for use as ingredients in the inventive compositions described herein.

In order to improve the adhesion characteristics, according to the invention, a vinyl chloride-acetate copolymer is added which has been modified with about 1% interpolymerized maleic acid. By way of example, the copolymer commercially available under the trade designation of VMCH as supplied by Bakelite Corporation, and Exon 470 as supplied by Firestone Tire and Rubber Company, may be used in these inventive compositions as the vinyl chloride-acetate copolymer modified with interpolymerized maleic acid. The presence of carboxyl groupings of the maleic acid accounts for the improved adhesion, but the chemical resistances tend to become somewhat diminished. Therefore, it is preferable to include both types of vinyl chloride-acetate copolymers to balance the chemical resistance of the first type with the adhesive characteristics of the second type. Too much of either component in the composition will result in either lack of adhesion or lack of adequate chemical resistance.

A chlorinated biphenyl, preferably of the 60% chlorinated plasticizer type, such as, for example, that supplied under the trade name Arochlor 1260 by Monsanto Chemical Company, is added to the composition to accomplish a threefold purpose: First—it increases the chemical resistance of the coating; Second—it provides enough flexibility to the coating to overcome the previously described tendency of the vinyl chloride resin to brittleness and flaking; and Third—it improves the solvent release of the vinyl copolymers. An excess of plasticizer, however, will tend to keep the film "open" and thus porous.

The inventive composition material may be manufactured to produce a clear coating, but for greater ease of visibility during and after application on a surface, opaque pigments, either white or colored, are preferably added.

In order to provide greater homogeneity to the film and to produce greater resistance to the erosion effect of hydrogen bubbling, to reduce tendency of the film to porosity and moisture penetration and to increase the speed of dry, I prefer to add to the composition one or more inert extender pigments, such as, for example, magnesium silicate, calcium silicate and the like. As an example of such an extender, magnesium silicate, or SF 399 Talc, supplied by Whittaker, Clark & Daniels has been used with success. Micronized talc such as Sierra Mistron may be substituted for the SF 399 Talc.

As a stabilizer to improve the packaged stability of the composition, according to the invention, I prefer to add propylene oxide. I have found that this compound stabilizes the inventive composition so that it can be stored for indefinitely long periods of time without deterioration or decrease in chemical resistances of the coatings formed therefrom.

The composition will contain, in addition to a resin of vinyl chloride type, a vinyl chloride-acetate copolymer modified with interpolymerized maleic acid, a chlorinated biphenyl plasticizer, and propylene oxide, a suitable solvent or solvent mixture whereby the essential ingredients will be blended and a solution or mixture formed of viscosity or fluidity such as to enable its application to a surface to be coated, as by brushing, spraying, dipping, or otherwise. The solvent or solvent mixture will desirably be of a volatile nature and will act as a vehicle, being wholly or largely dissipated by, for example, evaporation after application of the composition to a surface for the formation of a film. The solvent may be of any suitable type for the purpose, as for example, a mixture of methyl ethyl ketone, methyl isobutyl ketone and

toluol. Xylol may be substituted for toluol but will appreciably slow the drying time and may cause tail end precipitation or haze. The solvent will desirably be a solvent for other ingredients which may be included in the composition, and will be used in an amount with relation to the ingredients to be dissolved such as to give the viscosity or fluidity desired.

In addition to the essential ingredients, vinyl chloride-acetate copolymer, vinyl chloride-acetate copolymer modified with interpolymerized maleic acid, chlorinated biphenyl, an extender and stabilizer, the composition, as has been indicated, may also contain various other ingredients, as for example, pigments, etc. etc. Ingredients which may be included in the composition, in addition to those indicated as essential may be included in varying amount as may be dictated by the characteristics of the additional ingredients and the purpose for which the given composition is intended.

The proportions found most suitable are hereinafter set forth in Table I as an illustrative example contemplated by the instant invention, the percentages being by weight.

TABLE I

	Percent
25 Vinyl chloride-acetate copolymer-----	3.84
Vinyl chloride-acetate copolymer modified with about 1% interpolymerized maleic acid-----	9.94
Chlorinated biphenyl-----	3.84
Methyl ethyl ketone-----	19.20
30 Methyl isobutyl ketone-----	33.60
Toluol -----	14.92
Pigment -----	8.15
Extender (magnesium silicate talc)-----	6.40
Propylene oxide-----	0.11
55	100.00

It is to be understood that the proportions given in the above example are preferred, but that the proportions may be varied considerably, with and without ingredients other than those indicated herein as essential. Suitable proportions are from about 1.5% to about 6.3% vinyl chloride-acetate copolymer, about 6.3% to about 15.5% of the copolymer modified with interpolymerized maleic acid, about 2.0% to about 6.0% chlorinated biphenyl, about 10.0% to about 30.0% methyl ethyl ketone, about 10.0% to about 60.0% methyl isobutyl ketone, about 5.0% to about 20.0% toluol, about 2.0% to about 20.0% pigment, about 2.0% to about 14.0% extender, and about 0.05% to about 1.5% propylene oxide.

Considering only the essential ingredients and taking the proportionate content of the unmodified vinyl chloride-acetate copolymer (for example VYNS) as unity, suitable proportions of non-volatiles present in the composition in relation thereto may be varied approximately as follows with satisfactory results:

TABLE II

	Ratio
60 Vinyl chloride-acetate copolymer (VYNS)-----	1
Vinyl chloride-acetate copolymer modified with about 1% interpolymerized maleic acid (VMCH) -----	1.5-4.0
Chlorinated biphenyl (Arochlor 1260)-----	0.5-2.5
Extender (magnesium silicate)-----	0.5-4.5
65 Stabilizer (propylene oxide)-----	0.01-0.9
Solvents, as required.	

The content of solvents or volatile ingredients will be dependent upon the desired method of application, i.e. brushing, spraying, dipping, tumbling, rolling, troweling, etc.

A stopoff coating is preferably formed from the inventive composition in the following manner. For normal usage three coats are sprayed on the surface to be protected, allowing 20 minutes drying time between coats. The final coat is then baked at a temperature of approx-

imately 150° F. for one hour, or instead may be air-dried at room temperature overnight. A stopoff coating of sufficient thickness prepared in this manner will resist the action of an acid plating bath or anodizing bath for 48 hours or more. After the plating operation is completed, the stopoff coating is removed by common active ketone solvents. Vapor degreasers such as trichlorethylene, perchlorethylene, methylene chloride, and the like may be effectively utilized in addition to the ketone solvents in the removal operation.

As further examples of satisfactory compositions within the scope of the present invention, the following are disclosed, in addition to Example I listed in Table I:

Example II

Trade name	Supplier	Chemical designation	Approximate Composition by weight, percent
Exon 450.....	Firestone.....	Vinyl chloride copolymer.	4.00
Exon 470.....	do.....	do.....	9.78
Arochlor 1260.....	Monsanto.....	Chlorinated biphenyl.	3.84
Methyl ethyl ketone.	Shell Chemical.....	do.....	19.20
Methyl isobutyl ketone.	do.....	do.....	33.60
Toluol.....	do.....	do.....	14.92
Pigment.....	do.....	do.....	8.15
SF 399 talc.....	Whittaker, Clark & Daniels.	Magnesium silicate.	6.40
Propylene oxide.....	Union Carbide.....	do.....	0.11
			100.00

Example III

Trade name	Supplier	Chemical designation	Approximate Composition by weight, percent
VYNS.....	Bakelite.....	Vinyl chloride-acetate copolymer.	5.00
Exon 470.....	Firestone.....	Vinyl chloride copolymer.	7.50
Arochlor 1260.....	Monsanto.....	Chlorinated biphenyl.	3.50
Arochlor 5460.....	do.....	do.....	1.62
Methyl ethyl ketone.	Shell Chemical.....	do.....	19.20
Methyl isobutyl ketone.	do.....	do.....	33.60
Toluol.....	do.....	do.....	14.92
Pigment.....	do.....	do.....	8.15
SF 399 talc.....	Whittaker, Clark & Daniels.	Magnesium silicate.	6.40
Propylene oxide.....	Union Carbide Chemical.	do.....	0.11
			100.00

While I have described a specific application of the present invention, obviously many modifications and variations thereof 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.

I claim:

1. An organic solvent solution of a vinyl chloride water immiscible resin coating composition capable of drying at room temperature characterized by its ability to deposit a film showing marked resistance to acid chemical attack and abrasion and showing a high degree of adhesion to the surface covered thereby, said composition comprising, by weight, about 150 to about 400 parts vinyl chloride modified with about 1% interpolymerized maleic acid, about 50 to about 250 parts chlorinated biphenyl of 60% chlorination, about 50 to 450 parts of an extender, about 1 part to about 90 parts propylene oxide, about 100 parts of an unmodified vinyl chloride-vinyl acetate copolymer, and a volatile vehicle, the vinyl resins having been first dissolved in ketone solvents.

2. An organic solvent solution of a vinyl chloride water immiscible resin coating composition capable of drying at room temperature characterized by its ability to deposit a film showing marked resistance to acid chemical attack and abrasion and showing a high degree of adhesion to the surface covered thereby, said composition comprising, by weight, about 150 to about 400 parts vinyl chloride modified with about 1% interpolymerized maleic acid, about 50 to about 250 parts chlorinated biphenyl of 60% chlorination, about 50 to about 450 parts of a silicate extender, about 1 part to about 90 parts propylene oxide, about 100 parts of an unmodified vinyl chloride-vinyl acetate copolymer and a volatile vehicle.

3. A coating composition according to claim 2 and including an opaque pigment in an amount sufficient to impart opaqueness to a film produced from said composition.

4. An organic solvent solution of a water immiscible plating and anodizing stopoff coating composition capable of drying at room temperature comprising as principal film forming constituents an unmodified vinyl chloride-vinyl acetate copolymer and a vinyl chloride-vinyl acetate copolymer modified with maleic acid and containing as a plasticizer a chlorinated biphenyl of 60% chlorination in an amount, by weight, from about 2.0% to about 6.0%, and including about 0.5% to about 1.5% propylene oxide, about 2.0% to about 14.0% of a silicate type extender, about 2.0% to about 20.0% of an opaque pigment, and a volatile vehicle.

5. A coating composition according to claim 4, wherein said unmodified vinyl chloride-vinyl acetate copolymer is present in an amount, by weight, from about 1.5% to about 6.3% and said copolymer modified with maleic acid is present in an amount from about 6.3% to about 15.5%.

6. A coating composition according to claim 5, said volatile vehicle consisting essentially of about 10% to about 30%, by weight, of methyl ethyl ketone, about 10% to about 60% methyl isobutyl ketone, and about 5% to about 20% toluol.

7. An organic solvent solution of a non-aqueous stop-off composition for forming a stopoff masking film on selected portions of surface to be exposed to acids; said composition being capable of drying at room temperature and consisting substantially, by weight, of about 3.84% unmodified vinyl chloride-vinyl acetate copolymer, about 9.94% vinyl chloride-vinyl acetate copolymer modified with about 1% interpolymerized maleic acid, about 3.84% chlorinated biphenyl of 60% chlorination, about 19.2% methyl ethyl ketone, about 33.6% methyl isobutyl ketone, about 14.92% toluol, about 8.15% of an opaque pigment, about 6.40% magnesium silicate talc, and about 0.11% propylene oxide.

8. A method of masking and impeding the flow of ions onto and from selected portions of surfaces immersed in acid electroplating baths, anodizing baths, chemical etching baths and chemical milling baths, which comprises the steps of applying a plurality of coats of an organic solvent solution of a non-aqueous composition comprised of a major portion, by weight, of a blend of an unmodified vinyl chloride-vinyl acetate copolymer and vinyl chloride-vinyl acetate copolymer modified with interpolymerized maleic acid, and minor portions each of chlorinated biphenyl of 60% chlorination, an extender and propylene oxide in a volatile solvent onto said selected portions of said surfaces, drying each of said plurality of coats before applying a successive one of said coats, the ratio of the ingredients of said composition to the unmodified vinyl chloride-vinyl acetate copolymer being

1.5 to 4.0 for the modified vinyl chloride-vinyl acetate copolymer

0.5 to 2.5 for the chlorinated biphenyl

0.5 to 4.5 for the extender

0.01 to 0.9 for the propylene oxide.

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9. A method of masking selected portions of surfaces immersed in acid baths for selective chemical milling, etching, and the like, which comprises the steps of applying a plurality of coats of an organic solvent solution of a non-aqueous composition comprised of a major portion, by weight, of a blend of an unmodified vinyl chloride-vinyl acetate copolymer and vinyl chloride-vinyl acetate copolymer modified with interpolymers of maleic acid, and minor portions each of chlorinated biphenyl of 60% chlorination, an extender and propylene oxide in a volatile solvent onto said selected portions of said surfaces, the ratio of the ingredients of said composition to the unmodified vinyl chloride-vinyl acetate copolymer being

1.5 to 4.0 for the modified vinyl chloride-vinyl acetate copolymer
0.5 to 2.5 for the chlorinated biphenyl
0.5 to 4.5 for the extender
0.01 to 0.9 for the propylene oxide

air drying each of said coats for about 20 minutes before applying a successive one of said coats, and then air drying said plurality of coats to produce a film.

10. An organic solvent solution of a non-aqueous coat-

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ing composition capable of drying at room temperature, comprising essentially a water immiscible, unmodified vinyl chloride-vinyl acetate copolymer, a vinyl chloride-vinyl acetate copolymer modified with about 1% interpolymers of maleic acid and further containing chlorinated biphenyl of 60% chlorination and propylene oxide, the ratio of said ingredients to the unmodified vinyl chloride-vinyl acetate copolymer being

1.5-4.0 for the modified vinyl chloride-vinyl acetate copolymer
0.5-2.5 for the chlorinated biphenyl
0.01 to 0.9 for the propylene oxide.

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