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PROCESS FOR COATING COPPER WITH VINYL RESINS

George M. Powell, 3d, South Charleston, W. Va., and Earl F. Carlston, Arlington, Va., assignors to Carbide and Carbon Chemicals Corporation, a corporation of New York

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1 Claim. (Cl. 148—6)

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Vinyl resins which contain free hydroxyl groups attached to the macromolecule may be divided into two classes. One type of such resins, of which polyvinyl alcohol is an example, contains sufficient hydroxyl groups to be soluble in water. The partial esters and partial acetals of polyvinyl alcohol in which sufficient hydroxyl groups are left unreacted, are also dispersible in water. However, such water-soluble resins are relatively insoluble in organic solvents. Another class of hydroxylated vinyl resins are those which contain insufficient hydroxyl groups to be soluble or dispersible in water. In general, these latter resins are soluble in organic solvents, such as alcohols.

It has previously been proposed to render polyvinyl alcohol, and its water-soluble partial esters and acetals, insoluble in water by treatment of the resins with certain insolubilizing agents, such as compounds of metals of the 6th and 8th groups of the periodic tables.

It has now been found that the water-insoluble, hydroxylated vinyl resins may be rendered insoluble in organic solvents by heating them with a copper compound at high temperatures. The copper compounds do not embrittle the resins under these conditions, whereas, salts of iron, chromium, manganese, cobalt and nickel cause the resins to become brittle under severe heating.

In another method of practicing the invention, the copper compound is not employed directly, but the water-insoluble hydroxylated vinyl resin is applied as a film to a surface of metallic copper along with ammonia or an amine. The ammonia or amine apparently dissolves or chemically attacks some of the copper surface, and the dissolved copper appears to diffuse into the resinous film. On heating the film to a high temperature, insolubilization of the resin occurs as before, a protective coating on the copper surface being formed.

To secure the maximum insolubilization of the hydroxylated vinyl resin, the length of time the resin and copper compound are heated should be adjusted with respect to the temperature. At temperatures of 250° F. to 325° F., a baking time of at least one hour seems required; at 350° F., at least 30 minutes seems necessitated, but better results are secured by heating the resin and copper compound for at least 15 minutes at 400° F., or for 5 minutes at 500° F. At temperatures below 250° F., very little, if any, insolubilization of the hydroxylated vinyl resin occurs, although solutions of the resin in organic solvents often gel upon the addition of a copper salt; but such a phenomenon does not correspond to true insolubilization of the resin. The heat treatment at the proper temperatures in the presence of the copper compound also serves to increase the hardness, toughness, adherence and softening point of the film.

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The copper atom appears to be the agent effecting insolubilization, and the salt group or complex to which it is attached serves only as a means of incorporating the copper atom with the resin. Thus copper complexes, such as cuprammonium hydroxide and cuprammonium sulfate may be employed. Also, both organic and inorganic salts of copper have been tested and found effective. Copper acetate, copper 2-ethylhexoate, copper sulfate, copper chloride and copper nitrate, all caused insolubilization of hydroxylated vinyl resins on heating. Films containing copper acetate appeared to have the best resistance to water. The amount of the copper compound employed may be varied, but generally about five to twenty parts of the copper compound per one hundred parts of the hydroxylated vinyl resin are employed.

In the embodiment of the invention in which the hydroxylated vinyl resin is applied in solution form to a copper surface, and some of the copper solubilized or attacked by the ammonia or amines, many amines have been tested and found effective, the first eight listed below being more effective than the succeeding ones. These amines include diethanolamine, triethanolamine, morpholine, monoamylamine, dibenzylamine, di-2-ethylbutylamine, aniline, cyclohexylamine, N,N' dihydroxyethyl ethylenediamine, N,N' tetrahydroxyethyl ethylenediamine, hydroxyethyl diethyl amine, propylene diamine, triethylene diamine, ethylene diamine, p-phenylenediamine, monoethanolamine, monoisopropanolamine, di-2-ethylhexenyl amine, di-2-ethylhexyl amine and hexamethylene tetramine. The proportions of amine which may be employed may be varied from about 10 to 20 parts of amine per 100 parts of the vinyl resin. Smaller amounts of ammonia may be used, proportions of 6.5 to 20 parts of a 28% aqueous ammonia solution per 100 parts of resin being typical.

The types of hydroxylated vinyl resins to which this invention is applicable include water-insoluble, partially hydrolyzed polyvinyl esters, and water-insoluble polyvinyl acetal resins containing unreacted hydroxyl groups. The degree of hydrolysis of the former resins, that is, the percentage of ester groups of the macromolecule which are hydrolyzed to hydroxyl groups, may vary from about 10% to about 40%. These res-

ins may be manufactured by dissolving the polyvinyl ester in an inert, anhydrous solvent, such as acetone, toluene or methyl acetate, adding an anhydrous alcohol, such as methanol, in the calculated proportions to give the desired degree of alcoholysis (hydrolysis) and causing the reaction to occur in the presence of an acidic or alkaline catalyst at temperatures of 30° to 60° C. Typical polyvinyl esters which may be partially hydrolyzed include polyvinyl acetate, polyvinyl propionate, polyvinyl butyrate and polyvinyl benzoate.

Water-insoluble polyvinyl acetal resins containing unreacted hydroxyl groups may be made by known methods, such as by reacting polyvinyl alcohol with an aldehyde or simultaneously hydrolyzing a polyvinyl ester and reacting it with an aldehyde. For each resin, the degree of acetalization must be correlated with the type of aldehyde reacted so that water-insoluble products result. In general, the degree of acetalization must be higher, the lower the molecular weight of the aldehyde reacted, in order to form water-insoluble products. By the degree of acetalization is meant the percentage of hydroxyl groups, considering the polyvinyl acetal resin as a derivative of polyvinyl alcohol, which are reacted with aldehydes. The remaining hydroxyl groups are either unreacted or partially esterified. The following are examples of water-insoluble polyvinyl acetal resins containing unreacted hydroxyl groups:

Polyvinyl formal resins, approximately 95% acetalized, remaining hydroxyl groups substantially unreacted.

Polyvinyl formal resins, approximately 77.9% acetalized, 13.4% of hydroxyl groups unreacted, and 8.7% of hydroxyl groups esterified with acetic acid.

Polyvinyl acetal resins, approximately 85 to 94% acetalized, remaining hydroxyl groups substantially unreacted.

Polyvinyl propional resins, approximately 52 to 92% acetalized, remaining hydroxyl groups substantially unreacted.

Polyvinyl butyral resins, approximately 42 to 90% acetalized, remaining hydroxyl groups substantially unreacted.

Polyvinyl valeral resins, approximately 33 to 90% acetalized, remaining hydroxyl groups substantially unreacted.

Polyvinyl hexal resins, approximately 31 to 90% acetalized, remaining hydroxyl groups substantially unreacted.

On adding a copper compound to a solution of one of these hydroxylated vinyl resins, gelation of the solution is frequently observed. However, the hydroxylated vinyl resin is not converted to a form resistant to solvents until after the appropriate heat treatment. The cause of such gelation is not clearly understood, since gelled solutions often become fluid again upon adding an excess of the copper compound. Also, the gels may be liquefied by adding certain reagents, such as acetic acid, acetic anhydride, ammonia, amines, or ammonium acetate. The degree or tendency towards gelation also depends on the particular copper compound employed. For instance, cuprammonium hydroxide does not cause gelation of the resin solution when excessive amounts are avoided, but copper acetate causes gelation even in small amounts. However, the effectiveness of an insolubilizing agent cannot be judged by its effect on the consistency of solutions of the hydroxylated vinyl resins. For instance, solutions of these resins will gel when calcium acetate is added, but the resins containing this salt do not become insoluble on baking.

The tendency toward gelation upon the addition of a copper compound also varies with the particular vinyl resin which is dissolved. For instance, the polyvinyl acetal resins seem less sensitive than the partially hydrolyzed polyvinyl esters.

The invention finds its most useful embodiment in the application of hard, adherent and solvent-resistant coatings to various surfaces. Where materials other than copper are to be coated, such as surfaces of iron, tin plate, and zinc, a copper compound is included in the coating. In coating copper or copper plated surfaces, ammonia or an amine is included in the coating composition to dissolve or activate part of the copper necessary for insolubilization. Thus, the composition may be employed to coat copper wire, chemical apparatus made of copper, such as balance pans, and copper reaction vessels. Since the compositions have good electrical insulating properties, very useful wire enamels for copper wire may be formed containing a hydroxylated vinyl resin, ammonia or an amine, and a solvent. Such wire enamels may be applied in the customary manner, the final heat treatment being a very brief one at a temperature of 800° F.

The composition may also be applied to surfaces other than metal, which will withstand the heat treatment required. Thus, heavy grades of paper may be impregnated with a heat-resistant coating by spreading the hydroxylated vinyl resin and the copper salt over the surface, and then baking the paper for 30 to 60 seconds at 250° F., followed by a bake of about 5 to 10 seconds at 400° F. The compositions may also serve as solvent-resistant adhesives for joining articles of paper, cloth, wood, metal, leather and other materials.

The following examples will serve to illustrate the invention:

Example 1

A solution of the following composition was prepared:

	Parts
Partially hydrolyzed polyvinyl acetate (approximately 16% hydrolyzed)	9.6
Methyl acetate	17.9
Methanol	15.5
Diethylene glycol mono-butyl ether	32
Water	21
Ammonia (28% solution in water)	4

This composition was applied to a clean copper panel by spraying. Almost immediately the film became tinged with a bluish-green color indicating that the copper was being attacked by the ammonia. After drying the panel for about 10 minutes, it was placed in an oven at 400° F. for 12 minutes. After the heat treatment, the film of resin became much harder, tougher and more adherent, and it assumed a brownish tinge. The baked film showed excellent resistance to acetone and other ketones, to ethylene dichloride, to toluene, to alcohols and to transformer oil. Immersing the coated panel in boiling water for two days did not loosen or soften the film.

Example 2

The composition shown in Example 1 was sprayed over an iron panel which had been previously electroplated with a thin film of copper. After baking the panel for 10 minutes at 400°

F., a film resistant to acetone and boiling water was obtained.

Example 3

The composition of Example 1 was applied by spraying to an iron panel that had been copper plated by immersion in an acidified bath of copper sulfate. After baking the panel at 400° F. for 10 minutes, a film resistant to boiling water and to acetone was obtained.

Example 4

A copper strip was cleaned and then dip-coated with the following solution:

	Parts
Partially hydrolyzed polyvinyl acetate (approximately 16% hydrolyzed)	15
Methyl acetate	28
Methanol	57

After air-drying, the coated strip was immersed in a cuprammonium hydroxide solution previously prepared by dissolving copper in 28% aqueous ammonia, bubbling air free of carbon dioxide through the solution for 18 hours and then filtering. After an immersion of five minutes in the bath, the coated strip was removed and rinsed in water. There was no appreciable change in the solubility of the resin at this point, and it was readily soluble in acetone. Upon baking the strip at 400° F. for 15 minutes, a coating was obtained which was very resistant to acetone.

Example 5

The following composition was prepared:

	Parts
Partially hydrolyzed polvinyl acetate (approximately 29% hydrolyzed)	9.6
Methyle acetate	17.9
Methanol	15.5
Diethylene glycol mono-butyl ether	32
Water	21
Ammonia (28% solution in water)	4

This composition was applied to a clean copper panel by spraying. The film became tinged with a bluish-green color indicating that some of the copper was being attacked by the ammonia. After drying the panel, it was placed in an oven at 400° F. for 12 minutes. After the heat treatment, the film of resin became much harder, tougher and more adherent. The baked film showed outstanding resistance to acetone and other ketones, to ethylene dichloride, to toluene, to alcohols and to transformer oil. Immersing the coated panel in boiling water for two days did not loosen or soften the film.

Example 6

A solution of the following composition was prepared:

	Parts
Partially hydrolyzed polyvinyl acetate (approximately 16% hydrolyzed)	9.6
Methyl acetate	17.9
Methanol	15.5
Diethylene glycol mono-butyl ether	32
Water	21
Diethanolamine	3

This composition was applied to a clean copper panel by spraying. The film became tinged with a bluish-green color indicating that the copper was being attacked by the diethanolamine. After drying the panel, it was placed in an oven at 400° F. for 12 minutes. After the heat treatment, the film of resin became much harder, tougher and more adherent. The baked film showed good

resistance to acetone and other ketones, to ethylene dichloride, to toluene, to alcohols and to transformer oil. Immersing the coated panel in boiling water for two days did not appreciably loosen or soften the film.

Example 7

The following compositions were prepared:

	A	B
Polyvinyl partial butyral resin (approximately 70% acetalyzed with butyraldehyde)	*Parts* 15	*Parts* 15
Methanol	110	110
Diethylene glycol mono-butyl ether	100	100
Cupric acetate (10% aqueous solution)	14	
Water		14
Glacial acetic acid	1	1

Two panels of black iron were thoroughly cleaned and films of the above resin were deposited on the panels from the respective solutions. Both films were than baked at 400° F. for 20 minutes. The coating on panel A was much more resistant to acetone and to hot water than the coating on panel B.

Example 8

The following composition was prepared:

	Parts
Polyvinyl formal resin (approximately 77.9% acetalyzed 13.4% free hydroxyl groups and 8.7% ester groups)	30
Dioxane	175
Methanol	75
Cyclohexanone	220
Cupric acetate (10% solution in water)	15
Glacial acetic acid	1

This ccmposition was applied to a clean black iron panel and the coating then baked at 400° F. for 15 minutes. After baking, the coating was resistant to dioxane and methanol.

Example 9

This example illustrates the fact that the copper salts do not cause the hydroxylated vinyl resins to become brittle on baking as do other insolubilizing agents. To show this, films of equal thickness of a polyvinyl partial butyral resin, approximately 70% acetalyzed with butyraldehyde, containing various metal salts were cast on glass. The metal salts tested were copper acetate, manganese acetate, chromium acetate, cobalt acetate, nickel acetate, zinc acetate, lead acetate, and mercury acetate. Each film, as well as a control film, containing no metal salt was baked at 450° F. for 15 minutes. The amount of cupric acetate employed amounted to about 10% of the resin and the amounts of the other metal salts were based on the molar equivalents. This made a significant difference in the amounts employed of the metal salts computed on a weight basis only in the case of lead acetate and mercury acetate.

After baking the films they were removed from the panels by steaming. The control film of untreated resin and the cupric acetate treated resin had about equal adhesion and required a considerable steaming period to release them from the glass, whereas all the other films stripped easily. Observation of the films showed that only the film containing the copper salt was as flexible as the control film and all the other films were more brittle. The vast majority of them were too brittle to handle and broke on slight flexure.

Example 10

The following composition was prepared:

	Parts
Polyvinyl partial butyral resin	168
Triethylene glycol di(2-ethylhexoate)	68
Copper 2-ethylhexoate	10

This composition was dispersed on a heated roll mill to form a resilient, elastic sheet having a green color. On baking the sheet at 250° F. for one hour, it became insoluble in alcohol, but did not lose its elasticity and resilience. Other plasticizers may, of course, be substituted for the one illustrated herein, such as dibutyl sebacate, tricresyl phosphate and triethylene glycol di(2-ethylbutyrate).

Such compositions may be dissolved in solvents, such as alcohols, and applied to cloth. After baking the cloth, an alcohol-insoluble, flexible coating of reduced thermoplasticity and increased resistance to water is formed. The coated cloth may be fashioned into raincoats and other articles prior to the insolubilization treatment.

The foregoing examples are intended to illustrate the principles of the invention, and many variations in the compositions, other than as specifically shown, are included within the scope of the invention. For instance, dyes, pigments, waxes, oils, plasticizers, synthetic gums, elastomers, and synthetic resins, may be included in the compositions as is customary in compounding vinyl resin coatings.

We claim:

Process for coating articles having a copper surface which comprises applying to the copper surface, a solution containing an organic solvent, water, ammonia, and one of the group consisting of water-insoluble partially hydrolyzed polyvinyl esters, and water-insoluble polyvinyl acetal resins containing free hydroxyl groups, permitting the liquids of the solution to remain in contact with the copper surface until a bluish-green color is observed heating the applied coating at a temperature of at least 325° F., and forming an adherent, alcohol-insoluble film on said surface.

GEORGE M. POWELL, 3RD.
EARL F. CARLSTON.

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