

May 19, 1959

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2,887,405

PHERAL COATING WITH NITROGEN RESIN PRIMER

Filed Nov. 8, 1956

2 Sheets-Sheet 1

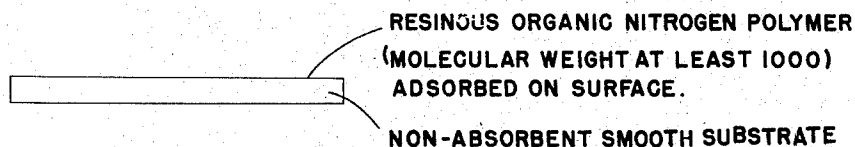


FIG. 1

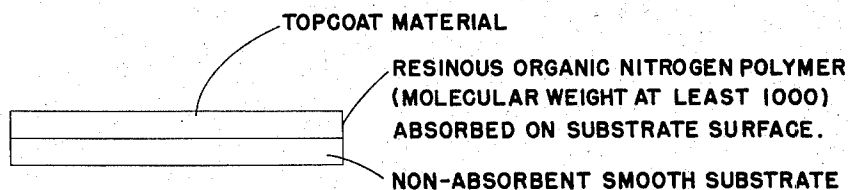


FIG. 2

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PERAL COATING WITH NITROGEN RESIN PRIMER

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2 Sheets-Sheet 2

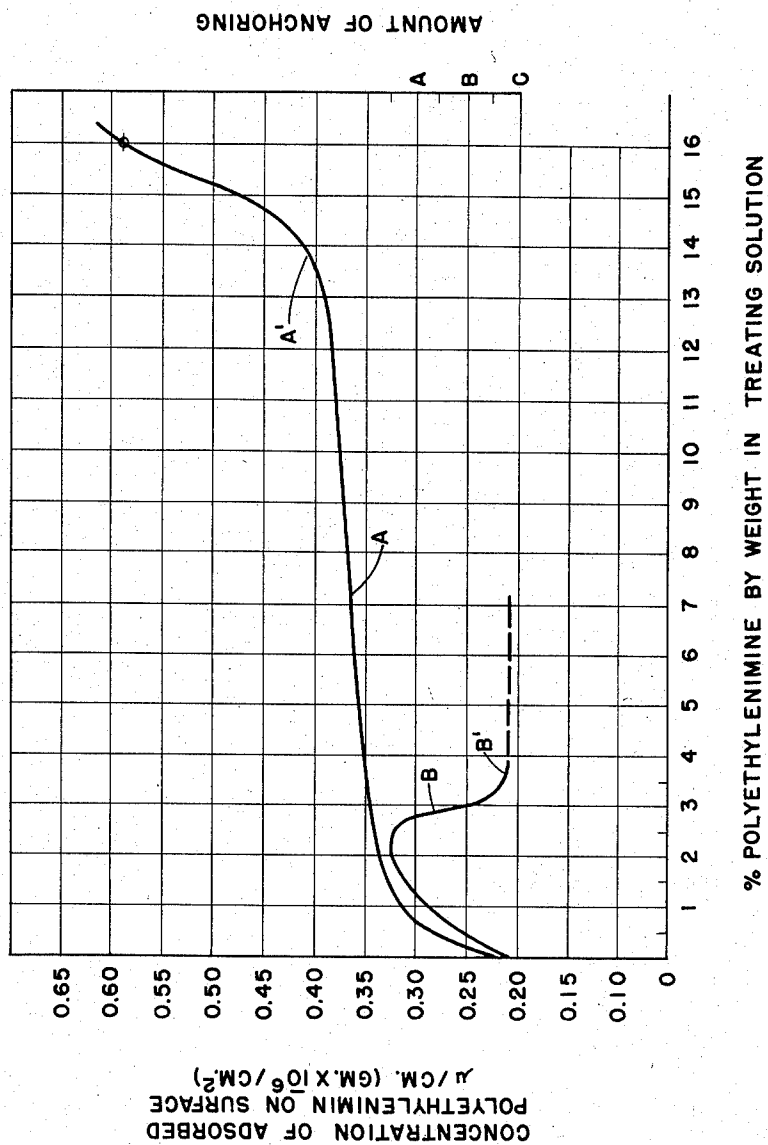
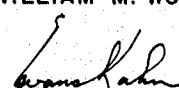


FIG. 3

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2,887,405

## PHERAL COATING WITH NITROGEN RESIN PRIMER

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Application November 8, 1956, Serial No. 621,174

15 Claims. (Cl. 117—81)

This is a continuation-in-part of my copending application Serial No. 541,841, filed on October 20, 1955.

This invention relates to the anchor coating or pretreatment of solid base (substrate) material principally for the purpose of obtaining stronger and more durable adhesion between the substrate and subsequently applied topcoating material. The invention is directed particularly to the pretreatment of substrates having a smooth, water-impermeable, non-porous surface to which topcoating material consequently adheres with difficulty, by depositing an anchor agent having a long-lasting effect on the substrate surface. The invention includes the treated substrates with and without topcoat material, and also methods whereby the anchoring agents and topcoat material are applied.

The securing of adequate adhesion of topcoat material to smooth or polished base material is a problem of long standing, particularly when the base material is flexible as in the case of foils, films or wire, or when the material is subject to scraping and denting as in the case of refrigerator boxes, automobile fenders, etc. It is particularly difficult to secure satisfactory adhesion in the case of base materials which are not merely apparently smooth but which are completely free from capillary pores and so have no "tooth." Surfaces of this smoothness are found on bright cold-rolled metal, clad metal, and electroplated metals; die drawn metal wire; metal foil; cast, compression molded, and extruded plastic masses; painted and lacquered surfaces; and cast or extruded hydrophobic organic film.

The aforementioned base materials are often topcoated. For example, in military service metals such as aluminum are frequently painted or lacquered to conceal their normal bright finish. In general service metals are generally painted or lacquered to prevent corrosion. The topcoat material may be an adhesive, as when aluminum foil is applied as over wood, plastics, paper, building board, etc. or may be fused organic material as when mylar, saran or polyethylene film is fused directly upon metal foil.

Nickel, tin, chromium and zinc are often similarly topcoated, particular when such metals are plated on steel or applied by hot-dip methods.

Small gauge copper wire intended for electrical use is often insulated by a thin coating of enamel.

Armed forces specifications generally require that all containers manufactured from tin plate be painted or lacquered on their outsides.

Rubber often carries topcoat material as when rubber cleats are cemented to the endless steel tracks of military tanks and agricultural vehicles, the topcoat material being the adhesive employed.

It is a principal object of the invention to improve adhesion of topcoat material to smooth base material for purposes such as those indicated above.

My parent application was based upon the discovery that the affinity of non-absorbent smooth base materials

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for organic topcoat material is greatly improved by an adsorbed surface content of a small but effective amount of a nitrogen compound as anchoring agent for the topcoat material.

The present invention is based upon two principal discoveries. The first is that surfaces treated with low molecular weight nitrogen compounds as described in my parent application, while possessing in most instances very satisfactory initial anchoring properties, lose these properties rapidly. I have found that such surfaces after aging for a few weeks or a few months are no better as regards anchoring than similar surfaces which have not been treated at all. My second discovery is that surfaces treated with or carrying high molecular weight nitrogenous products retain their anchoring properties apparently indefinitely.

Laboratory tests have shown that non-absorbent smooth surfaces having satisfactory and permanent anchoring properties generally result with the circumstances of the treatment are as follows.

(1) The amount of anchor agent present is small and preferably should be insufficient (as determined by the gravimetric test described below) to form a monomolecular layer on the surface of the substrate material. (2) The organic nitrogen compound has a molecular weight of at least 1,000. It will be understood in this connection that in certain instances the anchor agent may be applied in low molecular weight form and polymerized to high molecular weight form on the surface. (3) The ratio of the number of carbon atoms of the number of nitrogen atoms in the anchor agent is sufficiently low that the anchor agent presents a large number of points of attachment to the surface, and that the cationic effect of the nitrogen atoms be not unduly diluted. Effective anchoring appears to require that this ratio be not in excess of about 4:1. Thus good results have been obtained in the polymerized dimethylolurea where the ratio is 1.5:1 and in the case of polymerized trimethylolmelamine where the ratio is 1:1. Calculations show that anchoring agents of the type described contain as a rule at least about 10-20 nitrogen atoms per macromolecule. The number of nitrogen atoms in the macromolecule may be and usually will be much greater.

The substrates and topcoat materials improved include those listed above. The reason why these improvements occur in general or in any particular instance is not known, and I do not wish to be limited to any particular theory.

The agents used to impart anchoring according to the present invention are preferably hydrophilic (i.e., water-soluble or water-dispersible) high molecular weight resinous organic nitrogen polymers. They include both basic cationic nitrogen polymers and acidic anionic nitrogen polymers, and further include both groups of compounds in the form of their salts. The agents may be thermosetting polymers, particularly the cationic low molecular weight water-dispersible condensation products of such basic nitrogenous amidogens as urea, melamine, dicyandiamide, guanidine, formoguanamine, and biguanide with formaldehyde alone or in conjunction with modifying agents such as polyamine and polyalkylenepolyamines; or the polymers may be anionic such as the urea-formaldehyde-bisulfite resins and the resins prepared by condensing urea and formaldehyde in the presence of the lower water-soluble amino-alkyl carboxylic acids or the half esters of sulfuric acid with the lower water-soluble aminoalkanols. The agents may be employed in the form of their salts where more convenient.

In addition there may be used high molecular weight non-thermosetting cationic polyamines such as polyethylenimine; the resinous products formed by reacting

epichlorohydrin with ammonia, with alkyleneamines (for example ethylenediamine) or with polyalkylenepolyamines (for example 3,3'-iminobispropylamine and tetraethylenepentamine); or the resins formed by subjecting linear carbon chain resins carrying carboxamide substituents such as polymethacrylamide and 9:1 acrylamide: methyl acrylate copolymers to the Hofmann reaction whereby at least some of the amide groups are converted to amine groups resulting in formation of a polyamine resin. Still further, there may be employed polyvinylamine, polyvinylpyridine and polyalkylamine themselves. Mixtures of the above resins may also be used in the present specification.

For convenience the term "resinous polymer" will be used hereafter to designate compounds the high molecular weight nitrogen compounds used as anchor agents in the present invention.

As anchoring agents hydrophilic compounds are preferred because as a rule they are generally most conveniently and best applied from dilute aqueous solution, without need for organic solvents. The aqueous solution may contain between about 0.01% to 5% by weight of the anchor agent as needed to deposit a sufficient amount of the agent on the surface to be treated. An intermediate amount, e.g., between about 0.1% to 2% by weight of the agent or mixture of agents, is generally sufficient at contact times between 1/4 minute and 5 minutes. The solution is applied simply by contacting the substrate therewith, e.g., by dipping, spraying, roller coating or brushing. The surface of the substrate appears to adsorb the nitrogen base polymer very rapidly. Good results are obtained when the contact time is of the order of 3-5 seconds. Longer contact times may be used but in most instances are generally unnecessary, best results occurring when the surface carries not materially more than a substantially monomolecular film. A thicker film is often tolerated without however conferring corresponding improvement in adhesion.

It is possible to apply a layer of the anchoring agent of suitable thinness by dipping the substrate into a dispersion or solution of the anchoring agent of predetermined strength for a predetermined time and then removing and drying the substrate, so that only a very small amount is adsorbed. We have found it far easier, however, to immerse the substrate in a somewhat stronger solution of the anchoring agent and then to remove any excess anchoring agent present by washing the substrate with water. In most instances with anchor agent solutions of 0.1%-3% strength the step of rinsing the surface for a few minutes with plain water automatically leaves an approximately optimum amount of the anchor agent, substantially all of which appears to be in adsorbed form.

The invention will be further described with the reference to the drawings wherein:

Figure 1 is a vertical section of a horizontal sheet of substrate material showing schematically anchor resin of the present invention adsorbed on one surface thereof;

Figure 2 is a similar section showing the treated substrate of Figure 1 carrying subsequently applied topcoat material; and

Figure 3 shows two graphs, one (curve A) being a plot of the weight of polyethylenimine adsorbed by platinum on immersion in aqueous polyethylenimine solutions ranging from weak to strong, which plot shows gravimetrically the development of a monomolecular layer of the resin on the platinum, and the other (curve B) being a plot of the anchor strength developed by platinum sheets after similar treatment.

The data for curve A of Figure 3 were obtained by rendering 1" x 3" strips of sheet platinum perfectly clean (by degreasing with carbon tetrachloride, washing with deionized water, and heating to incandescence); weighing each strip with a quartz fiber microtorsion balance; immersing each strip for one to three seconds in an aqueous

polyethylenimine solution of the strength shown in the graph; rinsing the strips immediately thereafter for 5 minutes in running deionized water; drying the strips at 100° C. for 30 minutes, and reweighing the strips. From the weights obtained, the concentration of adsorbed polymer was calculated and plotted as hundredths of a  $\mu$ -gm. per square centimeter of platinum surface.

The data for curve B of Figure 1 were obtained by treating additional platinum strips in the same manner (except that the strips were dipped only halfway into the solution) and lacquering the strips with a standard laboratory test nitrocellulose lacquer when dried. The lacquer coatings were allowed to air dry for 48 hours and the anchoring properties possessed by the treated portion of the sheets were determined by the penknife test described in connection with Example 1 below.

Calculations and other data indicate that at a point A' of curve A (i.e., when the surface of the platinum contained about 0.40  $\mu$ -gm. of polyethylenimine per square centimeter), formation of a monomolecular layer of polyethylenimine on the surface of the platinum was substantially complete and that the second layer began at point A' or shortly thereafter. The results further show that even trace amounts caused some anchoring so that evidently there is no amount of polyethylenimine however small which will not produce at least some effect.

The results of curve B show that while significant anchoring took place when the concentration of polyethylenimine in the treating solution was very low, best anchoring occurred when the concentration of the polyethylenimine in the solution was about 2.5% and that the anchoring properties of the treated platinum declined to virtually zero when treating solutions containing 3.5% or more of polyethylenimine were employed.

Comparison of the results of graph B with the results of graph A show that at most only poor anchoring was obtained when the platinum carried a complete or nearly complete monomolecular layer of polyethylenimine. Comparison also shows that significant anchoring began when the platinum carried about a half completed monomolecular film (i.e., when the weight of adsorbed polyethylenimine was about 0.20  $\mu$ -gm. per square centimeter) and that best anchoring occurred when formation of the monomolecular layer was about 85% complete (i.e., when the weight of adsorbed polyethylenimine was about 35  $\mu$ -gm. per square centimeter). These and other data show that in general, for strongest anchoring, at least part of the surface, as determined gravimetrically as illustrated, should be free from anchoring agent, the remainder of the surface being covered by a substantially monomolecular layer of the agent.

The decline of curve B from its peak suggests that maximum anchoring effect required the exposure of about 15% of the surface of the platinum.

Treatment of platinum by the method described using 2.5% aqueous solutions of thermosetting amidogen-formaldehyde condensates described below failed to result in absorption of any weighable amount of the resin, although the treatment caused an excellent anchoring effect as determined by subsequent testing.

The evidence of the foregoing and other data is to the effect that the amount of anchoring agent present on a substrate before washing in most instances is principally a function of the concentration of agent in the solution, the temperature of the solution, the cleanliness of the surface, the polarity of the agent in the solution, the surface tension of the solution, and the molecular size or mobility of the agent therein. The amount of anchoring agent which gives optimum bonding may vary with the nature of the substrate and the anchoring agent. Evidently, in certain instances a layer of suitable thinness can be formed in one dipping step, without need for further treatment. As a result, the amount of agent which should be deposited in any one instance for best results, and whether excess agent is present requiring washing, are most easily

determined by laboratory trial employing the test methods shown in the examples. The presence of more agent than the optimum amount thus determined generally decreases the anchoring effect, as the excess acts as overlying loosely-attached layers, and thus in most instances the anchoring properties of the treated surface are improved by rinsing the surface with water.

The amount of anchoring agent applied according to preferred embodiments of the present invention should not be confused with coatings applied for decorative or protective purposes. Coatings applied for decorative purposes are only generally least about 0.5 mil in thickness and are at least about 3.5 mils thick when applied for protective purposes. In distinction, the amount of anchor agent preferably present according to the present invention is so small that the agent is nearly or completely invisible on metals such as polished aluminum, gold and platinum.

It is usually advantageous to dry the substrate following application of the anchoring agent. Somewhat better and more permanent anchoring generally results when the anchoring agent is a thermosetting resin and the drying is conducted under conditions leading to conversion of the resin to hydrophobic gel form. For the latter purpose it is usually sufficient to air-dry the substrate for some hours. Substantially complete polymerization with further improvement may result on heating the substrate at 80°–140° C. for a few minutes to half an hour.

In broad form, therefore, articles of manufacture embodying the invention may be defined as a base comprising a smooth nonabsorbent surface having adsorbed thereon a small but effective amount of a resinous organic nitrogen polymer having a molecular weight in excess of 1,000 as anchoring agent for subsequently applied topcoat material, the ratio of the total number of carbon atoms in the nitrogen polymer to the total number of nitrogen atoms of said polymer being not more than about 4:1.

The invention is broadly defined from the process aspect as the step of adsorbing the anchoring agent on the base material in small effective amount.

The anchoring agents of the present invention are defined as resinous organic nitrogen polymers having a molecular weight in excess of 1,000, the ratio of the total number of carbon atoms in the polymers to the total of nitrogen atoms therein being not in excess of 4:1. They may be applied in either polymerizable or non-polymerizable form. If applied in fully polymerized form, their molecular weight should be at least 1,000, as stated. Polymerizable agents applied in non-polymerized form (e.g., dimethylolurea, trimethylolurea) should be caused to polymerize to a molecular weight in excess of 1,000 after application to the surface, it being understood that the development of the requisite high molecular weight may be assisted by drying or curing the resin at an elevated temperature by the presence of an acid catalyst, or in appropriate instances by the use of a cross-linking agent (such as glyoxal in the case of polyamides).

Suitable high molecular weight non-polymerizable agents are illustrated by the water-soluble polyalkylenimines (linear chain polymers such as polyethylenimine, polypropylenimine composed of alkylenimine linkages), and by polyacrylamide treated according to the Hofmann reaction whereby some of the amide groups are converted to amino groups. Such polymers normally have molecular weights far in excess of 1,000. High molecular weight polymerizable agents are illustrated by the urea-polyalkylenepolyamine-formaldehyde resins, the polyurea-formaldehyde resins, the dicyandiamide-arylamine-formaldehyde resins, and the dimethylolurea sulfonate resins in normal hydrophilic form, during the preparation of which the reaction syrup has been subjected to an acid condensation step. These resins generally have a molecular weight in excess of 1,000 as prepared and in addition

undergo extensive polymerization after application when heated or aged.

The base materials of chief practical interest are the metals, organic plastics including film material, and rubber. Suitable metals include steel, aluminum, copper, tin, magnesium, nickel, brass, zinc, gold, silver and platinum. Metals such as aluminum which carry on adherent oxide film may be treated without removal of the film. The metals may be used in the form of their common alloys, and the metals may have acid or heat-treated surfaces such as parkerized or sherardized steel. Smooth organic substrates benefited by the present invention include artificial hydrophobic masses and hydrophobic synthetic flexible organic films, as well as painted and varnished surfaces, fingernails, etc. The artificial masses include cast polyethyl methacrylate and cast polystyrene, molded phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde compositions, and similar amidogen-formaldehyde compositions, cellulose acetate, extruded ethylene-dichloride-sodium polysulfide resin, and vulcanized rubber, particularly in the manufacture of and retreading of automobile and truck tires. In the latter instance, the tire and the tread stock are both regarded as substrate material and the adhesive joining the two is regarded as the mutual topcoat.

The topcoat material referred to above and included within the scope of the present invention is any organic material which has heretofore been applied to the substrates mentioned for the purpose of surface protection, decoration, adhesion, labeling, etc. Among the protective and decorative topcoat materials are thus paints, including latex (water base) paints, organic baking enamels represented by the alkyd-modified amine-aldehyde lacquers; nitrocellulose lacquers; red lead and zinc chromate anti-corrosive primers; tar; hot melt thermoplastic compositions including hot plastic anti-fouling paint for ships' bottoms; rubber including natural and synthetic rubbers, chlorinated rubber, and rubber hydrochloride; and water-resistant transparent film material including polyethylene, mylar, saran and cellulose acetate.

Among the adhesives are the animal, casein, starch, phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, polyvinyl-butyril, polymethyl acrylate, polyvinyl acetate, and phthalic acid-glycol glues. Topcoat materials used for labeling include lithograph and other printing inks and wax pencils.

The invention will be further illustrated by the examples which follow. These examples are embodiments of the invention and are not to be construed as limitations thereon. Parts are by weight unless otherwise stated.

#### Examples 1–10

The following illustrates the application of resinous organic nitrogen polymers as anchoring agents to various metal surfaces and the effect thereof in promoting adhesion of subsequently applied topcoat material.

The anchoring resins employed were the following.

No. 1—Methylol-carbamyl-polyazaalkane resin.—This resin was prepared by refluxing 131.2 g. of 3,3'-iminobispropylamine with 87.5 g. of 1,2-dichloroethane and 50 cc. of water for two hours to form a polyazaalkane of maximum practical chain length, after which 200 cc. of water was added. 156 g. of the resulting resinous syrup was neutralized with 37% hydrochloric acid and reacted with 84 g. of potassium cyanate at 75° C. to introduce carbamyl groups. To this condensate was added 162 g. of 37% aqueous formaldehyde and the mixture reacted for 15 minutes at 68° C.

No. 2—Urea-formaldehyde-triethylenetetramine cationic resin.—This resin was prepared according to the method of Example 1 of U.S. Patent No. 2,554,475.

No. 3—Urea-formaldehyde-bisulfite anionic resin.—This resin was prepared according to the method of Example 1 (sample 5) of U.S. Patent No. 2,559,578. A similar resin may be made by passing sulfur dioxide gas

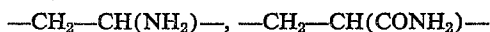
through aqueous dimethylolurea solution and then neutralizing; cf. Example 1 of U.S. Patent No. 2,407,376.

No. 4—*Melamine-formaldehyde acid colloid*.—This resin was prepared by mixing 220 g. of water, 480 g. of glycerol and 71 g. of 85% lactic acid, after which 100 g. of the spray-dried melamine-formaldehyde resin of U.S. Patent No. 2,345,543 was added with vigorous stirring until dissolved. The batch was aged for 18 hours before use.

No. 5—*Amphoteric vinyl tripolymer*.—The resin was prepared by mixing 80 g. of acrylamide, 5 g. of acrylic acid, 15 g. of N-methyl-2-vinylpyridine, 0.5 g. of ammonium persulfate and 400 cc. of water, heating the mixture at 80° C. for three hours, adding 62 g. of paraformaldehyde and reacting at pH 9 and 40° C. for one hour.

No. 6—*Quaternized triazine resin*.—This material was made by quaternizing 2-anilino-6-chloromethyl-4-phenyls-triazine with trimethylamine and forming a hydrophilic resinous methylol derivative by reacting the quaternary salt thus formed with three mols of 37% aqueous formaldehyde per mol of combined melamine present.

No. 7—*Acrylonitrile polymer*.—A water-soluble vinyl type polymer composed of



and  $-\text{CH}_2-\text{CH}(\text{CN})-$  linkages in about 6:4:10 molar ratio was prepared by a method of Example 6 of U.S. Patent No. 2,729,560 and reacted with one mol of formaldehyde per  $-\text{CONH}_2$  group present.

No. 8—*Polyethylenimine, prepared by homopolymerizing ethylenimine to a calculated molecular weight of 40,000 as calculated from its viscosity and sold under the name "Polymine P."*—Polymers substantially completely composed of recurring  $-\text{NH}-(\text{CH}_2)_x-$  linkages (wherein  $x$  represents an integer less than 4) having a molecular weight in excess of 10,000, are equivalents therefor.

No. 9—*Epichlorohydrin-tetraethylenepentamine resin*, prepared according to the procedure of Example 3 of Daniel et al. U.S. Patent No. 2,601,597.

No. 10.—10.0 g. (0.066 mol) of a polymerized p-chloromethyl styrene having a molecular weight of 85,000 (based on viscosity measurements) was dissolved in 190 g. of dioxane and 18.0 g. of trimethylamine added as a 25% aqueous solution (0.075 mol). The mixture was stirred for 12 hours at room temperature. The product was recovered by vacuum drying and analyzed N 3.5%, Cl. 7.4%. It contained about 17 quaternary groups per 100 linear chain carbon atoms. It easily dispersed in water forming a hazy colloidal cationic dispersion therein.

All resin solutions were adjusted to 0.5% resin solids by addition of water.

Anchoring baths were prepared by dissolving the above-described polymers in laboratory deionized water to give

solutions containing 1% resin solids by weight. Baths were also prepared at the same concentration using the chemical compounds shown in the table below. The baths were used at room temperature, without pH adjustment.

The commercial metals shown in the table below were tested in the form of cold-rolled laboratory panels 3" x 6" which were given no special treatment other than a wash in carbon tetrachloride to ensure access of the bath liquid. The rare metals (gold, silver and platinum) were tested in the form of sheets of heavy foil 4" x 8" which were similarly degreased.

One set of panels and one set of sheets of foil tested as follows. In each instance a panel or sheet of foil was treated by a 30-second dip half-way into an anchoring agent bath, draining at room temperature until dry, drying for 5 minutes at 200° F., flowing a commercial sea-blue nitrocellulose lacquer over the entire plate, and allowing the lacquer to dry at room temperature for 24 hours. The drying polymerized the thermosetting resins to molecular weights well in excess of 1,000. Adhesion of the lacquer coating in each instance was determined by a standard laboratory scratch test wherein the edge of a sharp pen-knife is scraped over the panel or foil with uniform pressure starting at the top or control (untreated) portion of the panel or foil and ending on the bottom or anchor agent treated portion. Sufficient pressure is applied to the knife blade to expose a path of bright metal about 1/8" in width over the control portion of the panel and this pressure is maintained as the knife blade passes over the anchor agent treated portion. The decrease in amount of lacquer removed from the latter portion under these conditions is a measure of the effectiveness of the anchoring agent.

Results are expressed on the scale A, B and C wherein C indicates that the amount of topcoat removed by the knife on both portions of the panel or foil was about the same and hence the absence of anchoring effect, B indicates only minor chipping of the topcoat and hence a moderate anchoring effect and A indicates only negligible chipping and hence a major anchoring effect. Plus and minus signs designate intermediate values. The rating of C+ designates the minimum improvement making the process economically worthwhile, whereas A+ designates a phenomenal improvement.

The results obtained are set forth below in the column headed "Dip."

A second set of panels was prepared in the same manner except that the panels and foil were washed with water for one minute after they had been dipped in the anchor agent bath and before they had been dried, so as to remove all unadsorbed (excess) anchoring agent. The results obtained on this set are shown below in the columns headed "Wash."

| Ex. No. | Anchor Resin No. | Aluminum |      | Magnesium |      | Steel |      | Park's'd Steel |      | Copper |      | Zinc |      |
|---------|------------------|----------|------|-----------|------|-------|------|----------------|------|--------|------|------|------|
|         |                  | Dip      | Wash | Dip       | Wash | Dip   | Wash | Dip            | Wash | Dip    | Wash | Dip  | Wash |
| 1       | 1                | A-       | A    | B+        | A    | C     | C+   | C              | C+   | C+     | A+   | B    | A-   |
| 2       | 2                | A        | A    | A+        | A+   | C+    | B+   | C+             | A+   | C      | A+   | B+   | A    |
| 3       | 3                | A        | A-   | A         | B+   | B     | A+   | B              | B+   | B      | A+   | B    | B+   |
| 4       | 4                | C        | B-   |           |      | C     | C+   |                |      | C      | A+   |      |      |
| 5       | 5                | C+       | B    | B+        | A    | C     | C+   |                |      | B      | B+   | B+   | A    |
| 6       | 6                | B        | B+   | B+        | A    | C+    | B    |                |      | B      | A+   | B    | A    |
| 7       | 7                | A        | A    | A         | A    | C     | B+   | C              | C+   | B+     | A    | A+   | A    |
| 8       | 8                | B        | A+   | B+        | A    | C     | B    |                |      | B+     | A    | B    | A+   |
| 9       | 9                | B        | B+   | B         | A    | B     |      |                |      | B+     | A    | B+   | A    |
| 10      | 10               | B        | B+   | B+        | A    |       |      |                |      | C+     | B    | B    | B+   |

| Ex. No. | Anchor Resin No. | Tin |      | Brass |      | Nickel |      | Gold |      | Silver |      | Platinum |      |
|---------|------------------|-----|------|-------|------|--------|------|------|------|--------|------|----------|------|
|         |                  | Dip | Wash | Dip   | Wash | Dip    | Wash | Dip  | Wash | Dip    | Wash | Dip      | Wash |
| 1.      | 1                | A-  | B-   |       |      |        |      |      |      |        |      |          |      |
| 2.      | 2                | C+  | B    | B+    | A-   | B      | A-   | A    | A    | A      | A    | A        | A    |
| 3.      | 3                | A+  | A+   | B+    | A    | A      | A    | A    | A    | A      | A    | A        | A    |
| 4.      | 4                | C   | C+   |       |      |        |      |      |      |        |      |          |      |
| 5.      | 5                | C+  | A    | B     | B+   |        |      |      |      |        |      |          |      |
| 6.      | 6                | A   | A-   |       |      |        |      |      |      |        |      |          |      |
| 7.      | 7                | B   | A    | B+    | A+   | B+     | A+   | B+   | A+   | B+     | A+   | B+       | A+   |
| 8.      | 8                | B   | A    |       |      |        |      |      |      |        |      |          |      |
| 9.      | 9                |     |      |       |      |        |      |      |      |        |      |          |      |
| 10.     | 10               |     |      |       |      |        |      |      |      |        |      |          |      |

In preparing the samples the panels were dipped into the anchoring baths for about half a minute. The results indicate that in most instances this was sufficient to substantially saturate the adsorptive capacity of the metal surfaces for the several agents.

The evidence of the table is that washing is necessary to achieve best results in the case of steel, parkerized steel, cooper, brass, and perhaps tin, and that washing is unnecessary in the case of the other metals tested. Evidently, the surface of this other group (aluminum, magnesium, zinc, etc.), permitted the excess resin to run off or collect in droplet form while the panels were being drained dry. The testing procedure was repeated after the panels had been allowed to age for 120 days. The ratings were substantially unchanged showing that polymers give comparatively permanent anchoring.

The foregoing procedure was repeated using the following monomeric low molecular nitrogen base compounds: n-hexylamine, ethylamine, secondary butylamine, hexylamine, diethylamine, trimethylamine, triethylamine, 2-aminoethanol, 2-chloroethylamine, diethylene-triamine, triethylenetetramine, tetraethylenepentamine, 3,3'-iminobispropylamine, phenethylamine, cyclohexylamine, ethylenediamine, pyridine, and aniline hydrochloride. Very satisfactory initial bonding was achieved in nearly every instance. The effect largely disappeared, however, after the samples had aged for 105-120 days.

#### Example 11

The anchoring agents of the present invention prolong the useful life of the red lacquer applied by housewives to their fingernails for purpose of decoration. This is illustrated by the following.

Four housewives were selected who regularly hand-washed family dishes. In making the test, the fingernails of the most used hand of each of the subjects were dipped into or swabbed with a 1/2% aqueous solution of the resins of Examples 1, 2, 7 or 8, and the fingernails of the other hand were treated with water in the same manner. All fingernails were allowed to dry for 20 minutes, after which the nails were painted with a commercial red nitrocellulose nail lacquer and allowed to air dry. The housewives then performed their normal duties.

The resins effected a major improvement in decreasing the size and frequency of lacquer chips. On the average, the untreated nails became so unsightly through chipping as to require touching up in about 48-72 hours, whereas the nails which carried anchoring resin remained satisfactory for 5-6 days. The resins of Examples 2 and 7 appeared to cause better anchoring than the resins of Examples 1 and 8.

#### Example 12

A series of steel panels was prepared to illustrate the effect of anchoring resins in decreasing the cracking of lacquer topcoat material which occurs when steel is sharply flexed.

The general procedure of Examples 1-10 was followed except that the resins were used in the form of 1/2% solutions and all panels were washed after application of

15 anchoring material. The topcoat material was the premium-grade white refrigerator enamel formed by dissolving a butyl methacrylate- $\beta$ -hydroxy ethyl methacrylate-styrene tripolymer in aromatic organic solvent along with guanamine-formaldehyde resin, and pigmenting the lacquer with titanium dioxide. The panels were baked at 400° F. for 30 minutes to cure the lacquer, and tested by flexing 180° over a 3/8" rod as mandrel. Results are as follows:

| Anchoring Agent  | Results                                                                    |
|------------------|----------------------------------------------------------------------------|
| None.....        | Many hair-line cracks along line of bend. Platelets of lacquer popped off. |
| Ex. 2 resin..... | No failure of lacquer.                                                     |
| Ex. 3 resin..... |                                                                            |
| Ex. 7 resin..... |                                                                            |
| Ex. 9 resin..... |                                                                            |

#### Example 13

The anchoring of a white lacquer applied over glossy organic articles is illustrated by the following.

Two dishes were molded from Bakelite BM-120 resin at 310° F. and 3000 p.s.i. and two from a commercial high-impact woodflour filled urea-formaldehyde molding composition. All four dishes were very dark in color. 40 Cylinders 3" in diameter were cast from styrene and methyl methacrylate. One set of the articles was treated with the resin of Example 2 and a second set with the resin of Example 9 in accordance with the procedure set forth above in connection with Examples 1-10. The products were rinsed with water, drained, dried at 40° C. overnight, flowed with white nitrocellulose lacquer, and dried for 24 hours at room temperature. Scrape tests made according to the method of Examples 1-10 showed that the lacquer on the treated portions of the articles had distinctly better anchorage.

#### Examples 14-23

The following illustrates the effect of a number of anchoring agents on glossy hydrophobic film. In this instance the topcoat material was applied in the form of an aqueous latex.

The films were anchor coated in general accordance with the procedure of Examples 1-10 except that the initial solvent cleaning step was omitted and the films were dried at room temperature after the dip in the anchor baths. The films were top coated by dipping into a latex prepared by copolymerizing a mixture of 55 parts of butyl acrylate, 43 parts of p-methylstyrene and 2 parts of methacrylic acid in 100 parts of agitated water at 90° C. containing anionic emulsifying agents and 0.7 part of ammonium persulfate catalyst. The films were then dried at 90° C. for 10 minutes.

The films were cut into 4" x 12" strips and tested by immersion in water maintained at 85° C. Failure was considered to occur when the topcoat began to slough off.

A second set of samples was prepared in the same manner except that the film was washed with water after immersion in the anchoring resin bath. Results were as follows.

| Ex.      | Anchor Resin No.   | Minutes to Slough  |       |                    |       |              |       |                 |       |                       |       |
|----------|--------------------|--------------------|-------|--------------------|-------|--------------|-------|-----------------|-------|-----------------------|-------|
|          |                    | Mylar <sup>1</sup> |       | Saran <sup>2</sup> |       | Polyethylene |       | Cellul. Acetate |       | Pliofilm <sup>3</sup> |       |
|          |                    | Dip                | Wash  | Dip                | Wash  | Dip          | Wash  | Dip             | Wash  | Dip                   | Wash  |
|          | Water <sup>4</sup> | 3.5                | ----- | 2                  | ----- | 1            | ----- | 7               | ----- | 4                     | ----- |
| 15.----- | 1                  | 3.5                | 15    | 3                  | 8     | 2            | 1.5   | 7               | 9     | 5                     | 11    |
| 16.----- | 2                  | 3.5                | 10    | 5                  | 12    | 3            | 3     | 7               | 8     | 7                     | 15    |
| 17.----- | 3                  | 3.5                | 11    | 2                  | 13    | 1            | 1.5   | 7               | 12    | -----                 | ----- |
| 18.----- | 4                  | 3.5                | 27    | -----              | ----- | 1            | 1.5   | -----           | 19    | -----                 | ----- |
| 19.----- | 5                  | 3.5                | 10    | -----              | ----- | 1            | 4     | 7               | 12    | 4                     | 9     |
| 20.----- | 6                  | 4                  | 11    | -----              | ----- | 2            | 3     | 7               | 14    | -----                 | ----- |
| 21.----- | 7                  | 3.5                | 27    | 6                  | 18    | 1            | 10    | 7               | 18    | 6                     | 19    |
| 22.----- | 8                  | 3.5                | 13    | -----              | ----- | 1            | 3     | 7               | 16    | -----                 | ----- |
| 23.----- | 9                  | 3.5                | 12    | -----              | ----- | 1            | 3     | 7               | 13    | -----                 | ----- |

<sup>1</sup> Terephthalic acid-glycol ester polymer.

<sup>2</sup> Vinylidene chloride-vinyl chloride copolymer.

<sup>3</sup> Chlorinated rubber.

<sup>4</sup> Control.

The term "saran" is a generic name for the homo- and copolymers of vinylidene chloride. Saran material within the scope of the definition may be employed in addition to the particular material described.

#### Example 24

The following illustrates application of the present invention in household painting.

A wooden cabinet many years old carrying many coats of high-gloss enamel was degreased by washing with carbon tetrachloride. Half of the cabinet was then sprayed with a 1% solution of the urea-formaldehyde-triethylenetetramine resin of Example 2, rinsed with water, and allowed to dry for several days. The entire cabinet was then painted with a high-gloss white kitchen enamel. When dry and hard, the enamel was tested by the knife test of Examples 1-10. Adhesion of the enamel was found to be much better on the area which carried anchor resin than on the untreated area.

The evidence of the table is that washing is necessary to achieve best results in the case of all five film materials tested.

#### Example 25

The anchor coating and top coating of smoothly glazed chinaware is illustrated by the following. Several glazed china saucers from a set of dinner-ware were anchor resin treated by the method of Examples 1-10, resins 2, 8 and 9 being employed, the saucers being rinsed with water being dipped into the anchoring resin solutions. The saucers were coated with nitrocellulose lacquer and tested in the same manner as described in Examples 1-10. Improved adhesion was observed in every case.

Additional saucers were treated with anchoring resin in the same manner and then were marked on the treated and untreated portions with the commercial red china-marking crayon known as Blaisdell No. 169. The plates were then immersed in warm water and the resistance of the marks to removal by smudging with the fingers observed. The marks on the anchor resin treated portions of the saucers were well retained long after the marks on the untreated portion had been removed. The foregoing results show that the adhesion of topcoat material including paint, asphalt, tar, etc. to concrete, plaster, gypsum board, cinder block, concrete block, bricks, etc. can be improved by treating the materials mentioned with anchoring resin according to the present invention.

#### Example 26

The anchoring agents of the present invention are of considerable use when the new synthetic thermoplastic transparent hydrophobic plastic sheet wrapping materials are heat sealed. This is illustrated by the following.

Strips of mylar (terephthalic acid-glycol ester polymer) were dipped in 0.5% aqueous solutions of the resin of Example No. 6, drained, and dried. Control strips were dipped in water and dried in the same manner. Hot press

20 trials were then made uniting sheets as follows: untreated to untreated; untreated to treated; and treated to treated. The sealing was performed in a laboratory press at a pressure of 10,000 lb./in. and a temperature of 200° C. The temperature of 200° C. was selected because at this temperature mylar does not form a strong seal and this magnifies the effect of variations in conditions.

25 The seals formed from the control sheets (A) could be separated readily with little effort. Considerably more effort was required to part the seals formed from the treated mylar.

#### Example 27

A smooth Connecticut fieldstone boulder was swabbed on one side with the resin of Example 7, washed with water, dried, sprayed with nitrocellulose lacquer, and air dried. The lacquer on the treated part of the stone showed superior adhesion when tested by knife scratch.

I claim:

1. As an article of manufacture a base comprising a non-absorbent smooth surface having adsorbed thereon a small but effective amount, less than a complete monomolecular layer, of a resinous organic nitrogen polymer having a molecular weight of at least 1,000 as anchoring agent, the ratio of the total number of carbon atoms in the nitrogen polymer to the total number of nitrogen atoms of said polymer being not in excess of 4:1.

2. An article according to claim 1 wherein the base material is metal.

3. An article according to claim 1 wherein the base material is steel.

4. An article according to claim 1 wherein the base material is aluminum.

5. An article according to claim 1 wherein the base material is a hydrophobic organic film.

6. An article according to claim 1 wherein the base material is magnesium.

7. An article according to claim 1 wherein at least about 5% of the surface, as determined gravimetrically, is free from anchoring agent, the remainder of the surface being covered by a substantially monomolecular layer of the anchoring agent.

8. As an article of manufacture a base comprising a non-absorbent smooth surface having adsorbed thereon a small but effective amount, less than a complete monomolecular layer, of a thermosetting urea-formaldehyde-bisulfite anionic resin dried beyond its gel point as anchoring agent.

9. As an article of manufacture a base comprising a non-absorbent smooth surface having adsorbed thereon a small but effective amount, less than a complete monomolecular layer, of a non-thermosetting linear chain polymer as anchor agent, said polymer being substantially completely composed of recurring linkages  $\text{—NH—(CH}_2\text{)}_x\text{—}$ , wherein  $x$  is an integer not in excess of 4, as anchoring agent, said polymer having a molecular weight of at least 10,000.

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10. As an article of manufacture a base comprising a non-absorbent smooth surface having adsorbed thereon a small but effective amount, less than a complete monomolecular layer, of a resinous organic nitrogen polymer having a molecular weight in excess of 1,000 as anchoring agent and carrying subsequently applied organic topcoat material thereover, the ratio of the total number of carbon atoms in the nitrogen polymer to the total number of nitrogen atoms of said polymer being not in excess of 4:1.

11. An article according to claim 10 wherein the topcoat material is a continuous organic film.

12. A process for improving a base comprising a non-absorbent smooth surface for subsequently applied topcoat material which comprises adsorbing on said surface from aqueous solution a resinous organic nitrogen polymer having a molecular weight in excess of 1,000 in small but effective amount as anchoring agent, the ratio of the total number of carbon atoms in the nitrogen polymer to the total number of nitrogen atoms of said polymer being not in excess of 4:1, the amount of polymer thus adsorbed being less than a complete monomolecular layer.

13. A process for improving a base comprising a non-absorbent smooth surface for subsequently applied topcoat material which comprises contacting said surface with an aqueous solution of a resinous organic nitrogen polymer having a molecular weight in excess of 1,000, the ratio of the total number of carbon atoms in the organic nitrogen polymer to the total number of nitrogen atoms in said polymer being not in excess of 4:1, until the adsorptive capacity of said surface for said polymer is substantially satisfied, and then washing said surface with water to remove unadsorbed nitrogen polymer present.

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14. A process for improving the adhesion of topcoat material to a non-absorbent smooth surface which comprises adsorbing on said surface from aqueous solution a small but effective amount of a resinous organic nitrogen polymer having a molecular weight in excess of 1,000 as anchoring agent and subsequently applying topcoat material thereover, the ratio of the total number of carbon atoms in the nitrogen polymer to the total number of nitrogen atoms of said polymer being not in excess of 4:1, the amount of polymer thus adsorbed being less than a complete monomolecular layer.

15. A process for improving the adhesion of topcoat material to a non-absorbent smooth surface which comprises contacting said surface with an aqueous dispersion of a thermosetting resinous organic nitrogen polymer having a molecular weight of at least 1,000 until the adsorptive capacity of said surface therefor is substantially satisfied, washing said surface with water to remove unadsorbed nitrogen polymer present, drying said surface to convert said polymer to thermoset form, and subsequently applying topcoat material thereover.

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