



RINSE AID FOR PLASTIC AND PAINTED SURFACES

BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a rinse aid for plastic and painted surfaces useful as a surface treatment of articles prior to painting thereof. In particular, the invention relates to certain polyphenol compounds formulated with surfactants, aqueous solutions of which provide a hydrophilic, antispotting rinse aid.

Description of Related Art

10 In the treatment of articles for subsequent painting or decorative coatings, including metals and plastics, the parts or articles are cleaned with conventional cleaner systems. Plastic and painted surfaces when cleaned with conventional, non-etching, acidic or alkaline cleaner systems, produce a hydrophobic, non-water wettable surface. This non-wettable surface is due to the hydrophobic nature of the surface being treated.

20 In copending, commonly assigned patent application--(Case No. P30065) Serial No. 07/128,673, filed 12/4/87, the treatment and after-treatment of metal with carbohydrate-modified polyphenol compounds is described. While a general reference to plastics is made in the field of the invention statement, the invention is described in relation to treatment of metal articles. Other metal treating patent applications and patents are also noted therein, the disclosure of which is expressly incorporated by reference, including issued U.S. Patents 4,517,028; 4,376,000; 4,433,015; and 4,457,790.

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DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as
5 modified in all instances by the term "about".

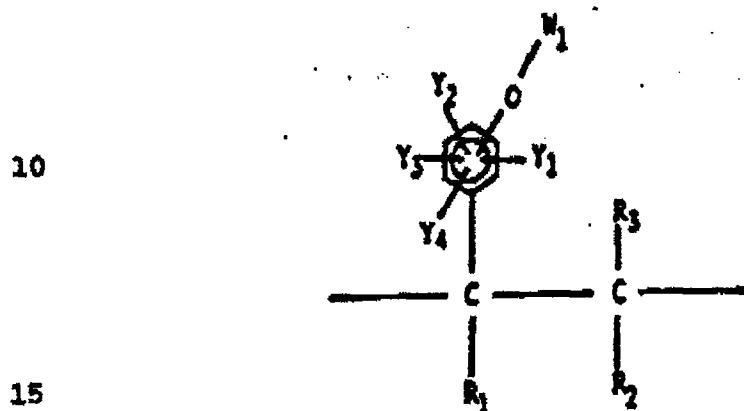
It has now been discovered that the derivative of polyphenol compounds can also be formulated for use in the treatment of plastic and painted articles which will eliminate water spotting by providing a water wettable surface and will
10 provide a visual indication of surface cleanliness and uniformity. After removal by current, conventional cleaner systems of soil, oil and contaminants followed by water rinsing, the plastic or painted article is then followed by treatment with a dilute aqueous solution of certain polyphenol
15 compounds. The surface following such treatment or rinse shows a water break-free surface after water rinsing and the residual film on the surface causes no loss of adhesion in subsequent paint operations.

As noted earlier, the polymers employed in the rinse aid
20 herein are certain polyphenol polymers. These may be generally described as a water soluble or dispersible polyvinylphenol polymers, containing polyhydroxyl alkylamine functionality resulting from the condensation of an amine or NH_2 with a ketose or aldose, followed by reduction to an amine,
25 [or other alkylaminopolyhydroxy compound having from about 3 to about 8 carbon atoms]. The polymers are employed in the form of an aqueous solution or dispersion thereof, or their salts. The aqueous dispersion or solution will contain an effective amount of the polymer to provide for a water wettable surface.
30 On a weight basis the polymer may be present in the working solution in a concentration by weight of the aqueous solution

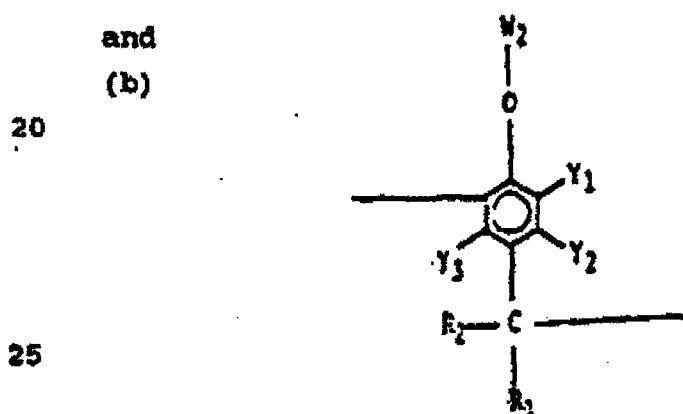
up to 5%, and preferably in the range of 0.001 to 1.0%.

The polymers employed in this invention are polymers, or copolymers thereof, synthesized from one or more monomers having a $-C=C-$ moiety, and having at least one unit of the formula (a) or (b) below:

(a)



and
(b)



wherein (a):

R_1 through R_3 are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, or an aryl group having about 6 to about 18 carbon atoms;

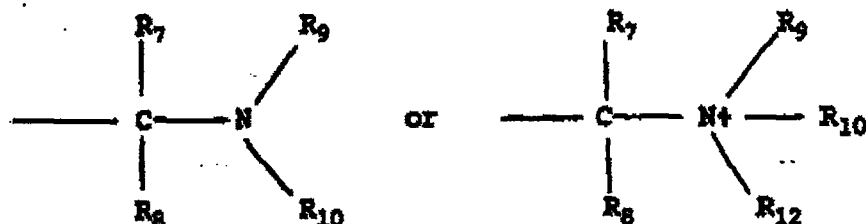


Y_1 through Y_4 are independently selected for each of said units from the group consisting of hydrogen, $-CR_{11}R_5OR_6$, $-CH_2Cl$, or an alkyl or aryl group having from 1 to 18 carbon atoms, or Z;

5

Z is

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however, at least a fraction of the Y_1 , Y_2 , Y_3 or Y_4 of the final compound or material must be Z and at least a fraction of said Z must contain a polyhydroxy alkyl-amine functionality resulting from the condensation of an amine or NH_3 and a ketose or aldose followed by reduction to an amine or other alkylaminopolyhydroxy compound having from about 3 to about 8 carbon atoms;

15

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R_5 through R_{12} are independently selected for each of said units from the group consisting of hydrogen, an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl, or phospho-alkyl moiety; R_{12} can also be $-O^{(-1)}$ or $-OH$, in order to form an amine oxide or a hydroxyl amine;

25

30

W_1 is independently selected for each of said units from the group consisting of hydrogen; an acyl moiety; an acetyl; a benzoyl moiety; 3-allyloxy-2-hydroxy-propyl-; 3-benzyloxy-2-hydroxy-propyl-; 3-alkylbenzyloxy-2-hydroxy-propyl-; 3-phenoxy-2-hydroxy-propyl-; 3-alkylphenoxy-2-hydroxy-propyl-; 3-butoxy-2-hydroxy-propyl; 3-alkyloxy-2-hydroxy-propyl; 2-hydroxyoctyl-; 2-hydroxy-alkyl-; 2-hydroxy-2-phenylethyl-; 2-hydroxy-2-



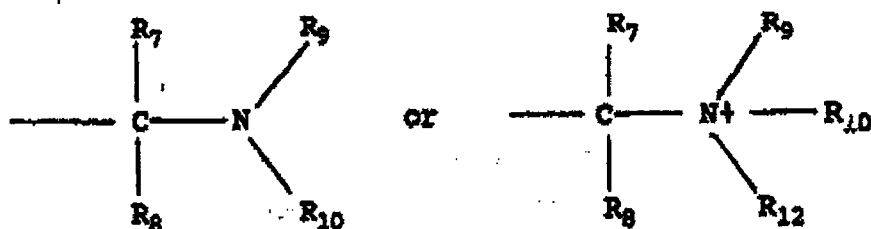
alkylphenylethyl-; benzyl-; methyl-; ethyl-; propyl-;
alkyl; allyl; alkylbenzyl-; haloalkyl-; haloalkenyl; 2-
chloro-propenyl-; sodium, potassium; tetra aryl ammonium;
tetra alkyl ammonium; tetraalkylphosphonium; tetraaryl
5 phosphonium; or a condensation product of ethylene oxide,
propylene oxide, a mixture, or copolymer thereof;
wherein in (b):

R_1 through R_2 are independently selected for each of
said units from the group consisting of hydrogen, an
10 alkyl group having from 1 to about 5 carbon atoms, or an
aryl group having from about 6 to about 18 carbon atoms;

Y_1 through Y_3 are independently selected for each of
said units from the group consisting of hydrogen,
15 $-CR_4R_5OR_6$, $-CH_2Cl$, an alkyl or aryl group having from 1
to 18 carbon atoms, or Z,



Z is



but at least a fraction of the Y_1 , Y_2 , Y_3 of the final compound must be Z, and at least a fraction of said Z must contain a polyhydroxy alkyl-amine functionality resulting from the condensation of an amine or NH_3 and a ketose or aldose followed by reduction to an amine, or other alkylamine polyhydroxy compound having from about 3 to about 8 carbon atoms.

R_4 through R_{12} are independently selected for each of said units from the group consisting of hydrogen, or an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl, or phospho-alkyl moiety; R_{12} can also be $-\text{O}^{(-1)}$ or $-\text{OH}$, in order to form an amine oxide or a hydroxyl amine;

W_2 is independently selected for each of said units from the group consisting of hydrogen; an acyl moiety; acetyl; benzoyl; 3-allyloxy-2-hydroxy-propyl-; 3-benzyloxy-2-hydroxy-propyl-; 3-alkylbenzyloxy-2-hydroxy-propyl-; 3-phenoxy-2-hydroxy-propyl-; 3-alkylphenoxy-2-hydroxy-propyl-; 3-butoxy-2-hydroxy-propyl; 3-alkyloxy-2-hydroxy-propyl-; 2-hydroxyoctyl-; 2-hydroxy-alkyl-; 2-hydroxy-2-phenyl-ethyl-; 2-hydroxy-2-alkyl-phenylethyl-; benzyl-; methyl-; ethyl-; propyl-; alkyl; allyl-; alkylbenzyl-; haloalkyl; haloalkenyl; 2-chloro-propenyl;



or a condensation product of ethylene oxide, propylene oxide, a mixture, or copolymer thereof.

Preferred final materials are based on a vinyl phenolic moiety or methyl vinyl phenolic moiety. For example, vinyl phenol, isopropenyl phenol and derivatives thereof may be used.

Illustrative of other polymers which are employed in this invention are copolymers materials (c) wherein at least one portion of said copolymer has the structure of (a) defined above wherein W_1 , Y_1 , through Y_4 and R_1 through R_{12} are as defined in (a) above and at least a fraction of said portion is polymerized with one or more monomers having a C=C moiety. Useful monomers include those independently selected for each of said units from the group consisting of acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide, n-amyl methacrylate, styrene, m-bromostyrene, p-bromostyrene, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, tert-butylamino-ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, n-butyl vinyl ether, tert-butyl vinyl ether, m-chlorostyrene, o-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-diallylmelamine, N,N-di-n-butylacrylamide, di-n-butylitaconate, di-n-butylmaleate, diethylaminoethyl methacrylate, diethyleneglycol monovinyl ether, diethyl fumarate, diethylitaconate, diethyl vinylphosphonate, vinylphosphonic acid, diisobutyl maleate, diisopropyl itaconate, diisopropyl maleate, dimethyl fumarate, dimethyl itaconate, dimethyl



maleate, di-n-nonyl fumarate, di-n-nonyl maleate, dioctyl fumarate, di-n-octyl itaconate, di-n-propyl itaconate, n-dodecyl vinylether, ethyl acid fumarate, ethyl acid maleate, ethyl acrylate, ethyl cinnamate,

5 N-ethylmethacrylamide, ethyl methacrylate, ethylvinyl ether, 5-ethyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine-1-oxide, glycidyl acrylate, glycidyl methacrylate, n-hexyl methacrylate, 2-hydroxypropyl methacrylate, isobutyl methacrylate, isobutyl vinyl ether, isoprene,

10 isopropyl methacrylate, isopropyl vinyl ether, itaconic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylolmethacrylamide, N-isobutoxymethylacrylamide, N-isobutoxymethylmethacrylamide,

15 N-alkyloxymethylacrylamide, N-alkyloxymethylmethacrylamide, N-vinyl-caprolactam, methylacrylate, N-methylmethacrylamide, o-methylstyrene, m-methylstyrene, o-methylstyrene, p-methylstyrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium p-styrenesulfonate, stearyl methacrylate, p-styrenesulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinylcarbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridine, 2-vinylpyridine N-oxide,

25 4-vinylpyrimidine, N-vinylpyrrolidone.

Within such materials, the ratio of any single monomer to any other monomer can be about 1:99 to about 99:1, preferably about 5:1 to about 1:5, and more preferably 1.5:1 to about 1:1.5.

30 Illustrative of another polymer which may be employed in this invention are condensation polymer



materials (a), which are a condensation polymer of polymer materials (a), (b), or (c), wherein condensable forms (i.e., modified as noted below) of (a), (b), or (c), or mixtures thereof, is condensed with a second compound selected from the group consisting of phenols (preferably phenol, alkylphenol, arylphenol, cresol, resorcinol catechol, pyrogallol), tannins, (both hydrolyzable and condensed) novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce a condensation resin product, that is a prepolymer of Polymer Material (d). This condensation resin prepolymer product is then further reacted by the addition of "Z" to at least a portion of it by reacting said resin prepolymer product with an aldehyde or ketone and a secondary amine producing a final adduct which can react with an acid and/or can be reacted with hydrogen peroxide to generate an amine oxide. The amine oxide can then be acid neutralized to form the hydroxyl amine if desired.

While this condensation product is described for convenience as being prepared by a sequential reaction, it will be appreciated that these materials can be prepared by carrying out the necessary steps in any order, or simultaneously. However, the sequence described is preferred.

It is appreciated by those skilled in the art, that the alkenylphenolic moieties of the present invention can be either randomly distributed within the copolymer and terpolymer or can be synthesized to constitute a block orientated polymer, depending upon the methods and conditions used for polymerization.



Preferred aldoses, ketoses, and derivatives for use in the above materials include, without limitation, glucose, fructose, alditols, aribanose, mannose, ribose, ribitol, and the like. Acids such as aldonic and aldonic acids may also be employed. Disaccharides and polysaccharides that can be easily hydrolyzed under reaction conditions to one or more of the useful aldoses and ketoses may also be employed.

It will be appreciated that the depiction above represents a repeating unit that characterizes the compound or materials of the present invention; no terminating end units are depicted. The end group not depicted of the polymers of the present invention can be selected by the skilled artisan relying upon art-disclosed techniques. For example, the end groups of the polymer may either be those resulting from the specific polymerization process employed or those intentionally added to alter the polymer characteristics. For example, the end groups may be hydrogen, hydroxyl, initiation fragments, chain transfer agents, disproportionation groups, or other similar methods of terminating a growing polymer chain.

The invention relates to the use of an aqueous solution or dispersion of the polymers in a process of treating plastic or painted surfaces by contacting said plastic or painted surface with the polymer solution. In the typical treatment employing the aqueous solution of polymer, the plastic or painted surface to be treated is initially cleaned and water rinsed to remove grease and dirt from the surface. The plastic or painted surface is then brought into contact with the treatment solution of



5 this invention usually by spraying. The treated surface is then water rinsed before being dried for example by air drying (forced air blow-off) or oven drying (flash drying in 200°F oven for about 60 seconds), although the treatment may also be applied without water rinsing with good results.

10 It is highly desirable, but not necessary, to provide or improve the water solubility or water dispersibility of the selected polymer material. In addition to employing the polyhydroxyalkyl-amine functionality, this is preferably done with an acid used for neutralization and/or complexation of a "Z" moiety thereof. Such acids may be organic or inorganic. Useful and preferred acids for this purpose include carbonic
15 acid, acetic acid, citric acid, oxalic acid, ascorbic acid, phenylphosphonic acid, chloromethylphosphonic acid; mono, di and trichloroacetic acid, trifluoroacetic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulfuric acid, boric acid, hydrochloric acid, hexafluorosilicic
20 acid, hexafluorotitanic acid, hexafluorozirconic acid, and the like. These may be employed alone or in combination with each other and may be neutralized by conventional acid-base reactions or by complexing. In a highly preferred embodiment, the addition of water to the
25 neutralized, overneutralized or partially neutralized treatment compounds mentioned above results in a water soluble or dispersible solution or emulsion of the polymer useful for treatment.

30 Alternately, the final polymer material, polyphenol compounds, used in the present invention can be made water soluble or dispersible by neutralization of the



phenolic group with an organic or inorganic base. Suitable bases for this purpose include tetra-alkylammonium hydroxides such as tetra-butylammonium hydroxide, tetra arylammonium hydroxide, sodium
5 hydroxide, potassium hydroxide and the like.

In a highly preferred embodiment, the final polymer material can be prepared such that the "Z" moiety does not require neutralization, i.e., an amine oxide or the like.

10 The molecular weight of the polyphenols used in the present invention can be a dimer, but may preferably be low molecular weight oligomers or resinous polymers having molecular weights in the range of about 360 to about 30,000. For use as a rinse aid as in the present
15 invention, the polymer of the formulas set forth hereinabove will typically have molecular weights in the range of about 1,000 to 15,000, with about 5,000 to about 15,000 being preferred.

20 As a rinse aid treatment composition the polymer is formulated with surfactants to produce a low foaming aqueous solution or dispersion. In the practice of this invention, the preferred surfactant employed is a mixture of an anionic surfactant and a nonionic surfactant to provide a low foaming aqueous dispersion which will
25 result in no spotting during the treatment and will provide a water break-free film after water rinsing. However, any surfactant which provides for low foaming may be employed, including anionic, cationic, amphoteric or nonionic surfactants. Typically in cleaning and
30 rinsing plastic or painted surfaces the water will bead up affording a non-continuous system rendering it



difficult to determine if the entire surface is clean from oil, fingerprints and the like to which subsequent painting would not adhere well. With the treatment of the present invention, a 100% water break-free film is provided after water rinse, which is a continuous water film showing no breaks and, accordingly, no portions of the surface to which paint would not subsequently adhere. In contrast to the 100% water break-free results of the present invention, a broken or discontinuous water film, either beads of water on the surface or spots with no water film, is designated as 0% water break-free, the broken film portions possibly having dirt, grime or oil spots over which the water does not provide a film.

The surfactants employed in this invention, are preferably mixtures of an anionic surfactant and a nonionic surfactant as noted earlier hereinabove. The surfactants must be water soluble or dispersible and preferably provide for low foaming.

The preferred anionic surfactants for use in the present invention are the alkyl sulfates, such as, sodium 2-ethylhexyl sulfate available commercially as Tergitol 08 from Union Carbide Corporation. Other anionic surfactants of this class are also available from the same supplier in which the alkyl portions of the surfactant contain up to about 18 carbon atoms. The preferred nonionic surfactants are the ethoxylated linear alcohols containing about 8 to 22 carbon atoms. Antarox LF 224 is of particular use in this invention which is an ethoxylated linear alcohol containing 8 to 10 carbon atoms and having a propylene oxide cap. Antarox nonionic surfactants are commercially available from General



5 Aniline and Film. Other nonionic surfactants are the alkyl and alkyl phenyl ethers of polyethylene glycols also available from Union Carbide under the Tergitol name, in which the alkyl group contains from about 8 to 12 carbon atoms. Illustrative cationic surfactants are the quaternary ammonium compounds, such as trimethyl coco quaternary ammonium chloride available commercially from 3herex under the name "Adogen". Illustrative of an amphoteric surfactant is Miranol JEM described as a 10 dicarboxylic octoic derivative sodium salt.

15 In preparing the rinse aid of the present invention, the surfactants are mixed and the polyphenol polymer added thereto. This is then added to water in an amount to provide the desired concentration for use as the rinse aid. As indicated, a mixture of anionic and nonionic 20 surfactant is preferred. The aqueous dispersion or solution of polymer will contain from on a weight basis about 0.001 to 5.0% polymer, as noted earlier. The surfactant, whether anionic, nonionic, cationic or amphoteric, will be present in an amount of 0.001 to 1% by weight.

25 In the method of using the rinse aid, the plastic or painted articles are first washed and rinsed, using conventional cleaning solutions. Illustrative of such cleaners are Parco Plastic Cleaner 2202, a potassium hydroxide, tetrapotassium pyrophosphate cleaner, and Parco Plastic Cleaner 2501, a phosphoric acid, monoammonium phosphate cleaner, available from Parker-Amchem Division of Henkel Corporation. The articles are 30 generally sprayed with the cleaner and rinsed with warm water after which the rinse aid of the present invention



is applied, usually by spraying, although other means of cleaning and rinsing may be employed such as immersion. After application of the rinse aid, the article is rinsed with water, preferably deionized water, and then dried by forced air or oven drying. The invention accordingly includes an improvement in the process of cleaning plastic or painted surfaces wherein a cleaner is applied thereto and rinsed and subsequently dried, the improvement being the application to the plastic or painted surfaces subsequent to the cleaning of said surfaces an aqueous solution or dispersion of the polymer described earlier above.

The invention is particularly useful in the treatment of plastic surfaces such as polycarbonates, polyurethanes and polyesters. The use of the rinse aid of the present invention ensures complete cleaning has resulted and will not detract from adhesion of paints applied to plastic surfaces afterwards, as results of testing show 100% adhesion.

The invention may be further illustrated by means of the following examples in which all parts and percentages are by weight unless otherwise noted.

EXAMPLE 1

This example will serve to illustrate the preparation of one polymer employed in this invention, the methyl glucamine derivative of a poly-4-vinylphenol polymer, as found in Example I of copending, commonly assigned application (Case No. P-30065) earlier noted.

A resin flask is charged with 400 mls Propasol P (a propoxylated propane solvent obtained from Union Carbide Corp., Danbury Connecticut) and 150g Resin M (a poly-4-



vinylphenol resin obtained from Maruzen Oil MW = 5000). A slurry of 263.3g N-methylglucamine in 400 mls deionized water is added, and the mixture is warmed to 60-65°C while stirring. Next, 100.2 mls of 37% formaldehyde is added over one and one-half hours. The mixture is then warmed to 90°C and held for six hours. After cooling, the mixture is diluted to 9.6% solids with deionized water. The pH of the final solution is 9.1 and the solution comprises an N-methyl-glucamine derivative.

EXAMPLE 2

The polymer solution of Example 1 was formulated with surfactants to provide a low foaming aqueous dispersion in water. Thus 975.0 parts of the polymer solution were added to a previously combined mixture of 18 parts of Tergitol 08 (an anionic surfactant, sodium 2-ethylhexyl sulfate) and 7 parts of Antarox 224 (a nonionic surfactant, an ethoxylated C₈₋₁₀ linear alcohol having a propylene oxide cap). An aqueous solution of the foregoing was prepared in deionized water by adding and mixing the foregoing with 400 parts water to provide a concentration of polymer by weight of 0.023%, and a concentration of surfactant by weight of 0.0045%.

EXAMPLE 3

The formulated rinse aid was then tested using primed plastic parts. The panel cleaning and testing of the rinse aid was performed using the following test cycle:



1. Parco Plastic Cleaner 2202 - 90 second spray
at 3 oz/gal at 125°F
- or
- 5 Parco Plastic Cleaner 2501 at 4% - 90 second spray
by volume at 125°F
2. Warm water (110°F.) rinse - 30 second spray
3. Rinse aid polymer at - 30 second spray
0.25% v/v at 80°F.
- 10 4. Deionized water rinse - 30 second spray
5. Forced air blow off

The cycle was carried out both with the rinse aid step 3 and without the rinse aid step. All panels processed without the polymer rinse aid showed 0% water break-free after rinsing. All panels processed with the polymer
15 rinse aid showed 100% water break-free after rinsing.

EXAMPLE 4

After drying of the panels treated in Example 3, the panels were painted with a paint using BASF Inmont 8L
20 395094-Basf® Coat/Clear Coat system. The panels were allowed to age at ambient conditions for a minimum of 72 hours before adhesion testing was conducted. Adhesion testing on the painted panels was evaluated under the following conditions.

- 25 a. After oven aging 7 days at 70°C
- b. After 96 hours at 100°F/100% relative humidity
- c. After 2 hours 100°F water immersion
- d. After a moisture and cold cycle test
- e. After 3 months and 1 year Florida exposure.

30 All the tests showed 100% adhesion on both the treated and non-treated panels illustrating that the

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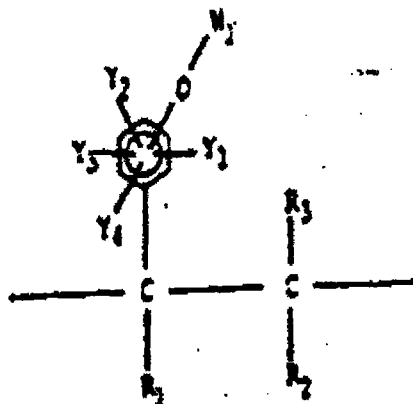
treatment did not interfere with the adhesion of paints to the panels and that the rinse aid showing 100% water break-free provided assurance that no oil or grease was left on the panels after cleaning.

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CLAIMS

1. A composition adapted for use as an aqueous rinse aid solution or dispersion in the treatment of plastic or painted surfaces comprising a surfactant and a water dispersible or soluble polyphenol polymer containing a polyhydroxyl alkylamine functionality resulting from the condensation of an amine or NH_3 with a ketose or aldose followed by reduction to an amine or other alkylaminohydroxy compound having from about 3 to about 8 carbon atoms.
2. A composition as defined in claim 1 wherein said polyphenol polymer has at least one recurring unit selected from the group consisting of
(a)



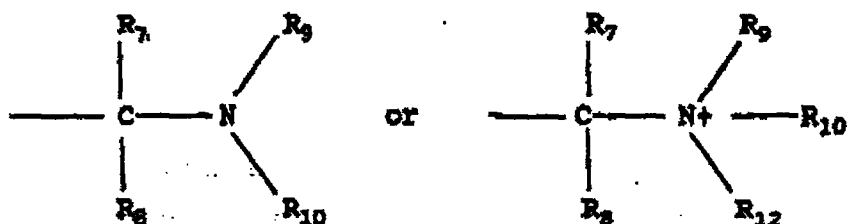
where:

R_1 through R_3 are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, or an aryl group having about 6 to about 18 carbon atoms; said units from the group consisting of hydrogen,



$-\text{CR}_{11}\text{R}_5\text{OR}_6$, $-\text{CH}_2\text{Cl}$, or an alkyl or aryl group having from 1 to 18 carbon atoms, or Z;

Z is



and, at least a fraction of the Y_1 , Y_2 , Y_3 or Y_4 of the final compound or material must be Z and at least a fraction of said Z must contain a polyhydroxy alkyl-amine functionality resulting from the condensation of an amine or NH_3 and a ketose or aldose followed by reduction to an amine or other alkylaminopolyhydroxy compound having from about 3 to about 8 carbon atoms;

R_5 through R_{12} are independently selected for each of said units from the group consisting of hydrogen, an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl, or phospho-alkyl moiety; R_{12} can also be $-\text{O}^{(-1)}$ or $-\text{OH}$, in order to form an amine oxide or a hydroxyl amine;

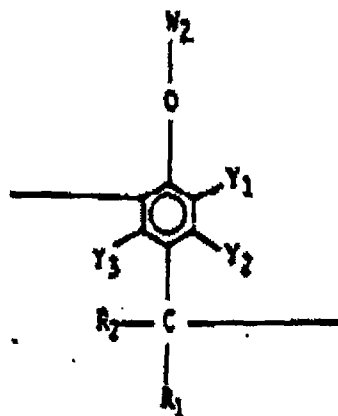
W_1 is independently selected for each of said units from the group consisting of hydrogen; an acyl moiety; an acetyl; a benzoyl moiety; 3-allyloxy-2-hydroxy-propyl-; 3-benzyloxy-2-hydroxy-propyl-; 3-alkylbenzyloxy-2-hydroxy-propyl-; 3-phenoxy-2-hydroxy-propyl-; 3-alkylphenoxy-2-hydroxy-propyl-; 3-butoxy-2-hydroxy-propyl; 3-



alkyloxy-2-hydroxy-propyl; 2-hydroxyoctyl-; 2-hydroxy-alkyl-; 2-hydroxy-2-phenyl ethyl-; 2-hydroxy-2-alkyl phenyl ethyl-; benzyl-; methyl-; ethyl-; propyl-; alkyl; allyl; alkyl benzyl-; haloalkyl-; haloalkenyl; 2-chloro-propenyl-; sodium, potassium; tetra aryl ammonium; tetra alkyl ammonium; tetra alkyl phosphonium; tetra aryl phosphonium; or a condensation product of ethylene oxide, propylene oxide, a mixture, or copolymer thereof;

and

(b)



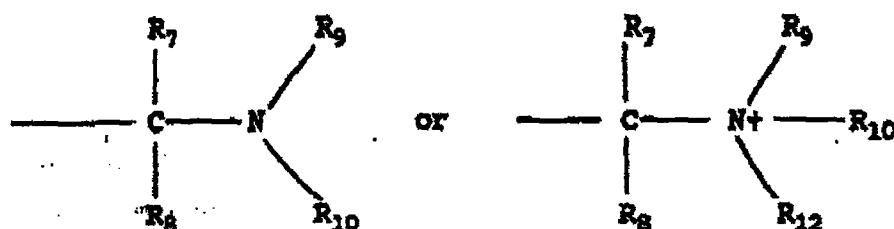
wherein:

R_1 and R_2 are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, or an aryl group having from about 6 to about 18 carbon atoms;

Y_1 through Y_3 are independently selected for each of said units from the group consisting of hydrogen, $-CR_4R_5OR_6$, $-CH_2Cl$, an alkyl or aryl group having from 1 to 18 carbon atoms, or Z,



Z is



but at least a fraction of the Y_1 , Y_2 , Y_3 of the final compound must be Z, and at least a fraction of said Z must contain a polyhydroxy alkyl-amine functionality resulting from the condensation of an amine or NH_3 and a ketose or aldose followed by reduction to an amine or other alkylaminopolyhydroxy compound having from about 3 to about 8 carbon atoms;

R_4 through R_{12} are independently selected for each of said units from the group consisting of hydrogen, or an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl, or phospho-alkyl moiety; R_{12} can also be $-\text{O}^{(-1)}$ or $-\text{OH}$, in order to form an amine oxide or a hydroxyl amine;

W_2 is independently selected for each of said units from the group consisting of hydrogen; an acyl moiety; acetyl; benzoyl; 3-allyloxy-2-hydroxy-propyl-; 3-benzyloxy-2-hydroxy-propyl-; 3-alkylbenzyloxy-2-hydroxy-propyl-; 3-phenoxy-2-hydroxy-propyl-; 3-alkylphenoxy-2-hydroxy-propyl-; 3-butoxy-2-hydroxy-propyl-; 3-alkyloxy-2-hydroxy-propyl-; 2-hydroxyoctyl-; 2-hydroxy-alkyl-; 2-



hydroxy-2-phenyl-ethyl-; 2-hydroxy-2-alkyl-phenylethyl-; benzyl-; methyl-; ethyl-; propyl-; alkyl; allyl; alkylbenzyl-; haloalkyl-; haloalkenyl; 2-chloro-propenyl-; or a condensation product of ethylene oxide, propylene oxide, a mixture, or copolymer thereof;

(c) a copolymer material wherein at least one portion of said copolymer has the structure of (a) defined above wherein W_1 , Y_1 through Y_4 and R_1 through R_{12} are as defined in (a) above and at least a fraction of said portion is polymerized with one or more monomers independently selected for each of said units from the group consisting of acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide, n-amylmethacrylate, styrene, m-bromostyrene, p-bromostyrene, pyridine, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, tert-butylamino-ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, n-butyl vinyl ether, tert-butyl vinyl ether, m-chlorostyrene, o-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-di-n-butylacrylamide, di-n-butyl itaconate, di-n-butyl maleate, diethylaminoethyl methacrylate, diethyleneglycol monovinyl ether, diethyl fumarate, diethyl itaconate, diethyl vinylphosphonate, vinylphosphonic acid, diisobutyl maleate, diisopropyl itaconate, diisopropyl maleate, dimethyl fumarate, dimethyl itaconate, dimethyl maleate, di-n-nonyl fumarate, di-n-nonyl maleate, dioctyl fumarate, di-n-octyl itaconate, di-n-propyl itaconate, n-dodecyl vinyl



ether, ethyl acid fumarate, ethyl acid maleate, ethyl acrylate, ethyl cinnamate, N-ethylmethacrylamide, ethyl methacrylate, ethyl vinyl ether, 5-ethyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine 1-oxide, glycidyl acrylate, glycidyl methacrylate, n-hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, isobutyl methacrylate, isobutyl vinyl ether, isoprene, isopropyl methacrylate, isopropyl vinyl ether, itaconic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylolmethacrylamide, N-isobutoxymethylacrylamide, N-isobutoxymethylmethacrylamide, N-alkyloxymethylacrylamide, N-alkyloxymethylmethacrylamide, N-vinyl-caprolactam, methylacrylate, N-methylmethacrylamide, α -methylstyrene, m-methylstyrene, o-methylstyrene, p-methylstyrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium p-styrenesulfonate, stearyl methacrylate, p-styrenesulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinylcarbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridine, 2-vinylpyridine N-oxide, 4-vinylpyrimidine, N-vinylpyrrolidone;

and (d) a condensation polymer of polymer materials (a), (b), or (c), wherein a condensable form of (a), (b), (c), or a mixture thereof, is condensed with a second compound selected from the group consisting of phenols, tannins, novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce a



condensation resin product, said condensation resin product then being further reacted by the addition of "2" to at least a portion of it by reacting said resin product with (1) an aldehyde or ketone and (2) a secondary amine producing a final adduct which can react with an acid.

3. A composition as defined in claim 2 wherein said polyphenol polymer is a poly-4-vinylphenol polymer.
4. A composition as defined in claim 1 wherein said composition has added to it a surfactant mixture of an anionic and a nonionic surfactant.
5. A surfactant mixture as defined in claim 4 wherein said anionic surfactant is an alkylsulfate having from about 8 to 18 carbon atoms and said nonionic surfactant is an ethoxylated linear alcohol having from about 8 to about 22 carbon atoms.
6. A surfactant mixture as defined in claim 5 wherein said alkyl sulfate is sodium 2-ethyl hexyl sulfate and said ethoxylated linear alcohol containing 8 to 10 carbon atoms.
7. A composition as defined in claim 4 in which, when added to water as a rinse aid solution, said poly-4-vinylphenol polymer comprises about 0.001 to about 5% by weight of the composition and said surfactant mixture comprises about 0.001 to about 1% by weight.

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8. A composition as defined in claim 7 in which said polymer is the Mannich derivative of N-methyl glucamine, formaldehyde and 4-vinylphenol of about 5,000-15,000; molecular weight and said anionic surfactant is sodium 2-ethylhexyl sulfate and said nonionic surfactant is an ethoxylated C₈₋₁₀ alcohol.
9. An aqueous solution or dispersion of the composition defined in claim 2 wherein said polymer is present in an amount of about 0.001 to about 5% by weight.
10. An aqueous solution or dispersion of the composition defined in claim 8 wherein said polymer is present in an amount of about 0.001 to about 1% by weight.
11. In a method of treating plastic or painted surfaces prior to subsequent painting thereof wherein said surfaces are cleaned and rinsed by application of a cleaning solution thereto and dried prior to painting, the improvement wherein subsequent to said cleaning and prior to drying said surfaces are contacted with an aqueous rinse solution of a surfactant and a water dispersible or soluble polyphenol polymer resulting from the condensation of a polyphenol, aldehyde such as formaldehyde and a polyhydroxyl alkylamine functionality resulting from the condensation of an amine or NH₃ with a ketose or aldose followed by reduction to an amine or other alkylaminohydroxy compound having from



about 3 to about 8 carbon atoms, in which said aqueous

solution contains said polymer in a concentration of about 0.001 to about 5% by weight.

12. In a method as defined in claim 11 wherein said polyphenol is a poly-4-vinylphenol polymer.
13. In a method as defined in claim 11 wherein said polymer is the Mannich derivative of a polymer of N-methyl glucamine formaldehyde and poly-4-vinylphenol.
14. In a method as defined in claim 11 wherein said aqueous solution of said polymer further contains surfactant(s).
15. In a method as defined in claim 14 wherein said surfactant is a mixture of an anionic and nonionic surfactant.
16. In a method as defined in claim 15 wherein said anionic surfactant is sodium 2-ethylhexyl sulfate and said nonionic surfactant is an ethoxylated alcohol having from 8 to 10 carbon atoms.
17. In a method as defined in claim 11 wherein subsequent to said contact with said aqueous solution containing said polyphenol polymer said surface is rinsed with deionized water prior to drying.
18. In a method as defined in claim 17 wherein said drying is air blown drying.