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Señores
**DIVISIÓN DE NUEVAS CREACIONES**
**SUPERINTENDENCIA DE INDUSTRIA Y CC**
**E. S. D.**

**REF.** Expediente No. **07-039.467**
Patente de Invención: **"MATERIALES DE EMBALAJE RECUBIERTOS"**
Solicitante: **PPG INDUSTRIES OHIO, INC.**

***DESTINO: 186***
**-SUSTITUCION PODER-**

**MARCELA GÓMEZ RUBIO,** mayor de edad, identificada con la cédula de ciudadanía No. 52.886.586 de Bogotá, Abogada en ejercicio portadora de la Tarjeta Profesional No. 137950 del Consejo Superior de la Judicatura, domiciliada en la Carrera 7 No. 74-64, Oficina 506 de Bogotá D.C., Colombia, actuando en caracter de apoderada de la sociedad **PPG INDUSTRIES OHIO, INC.,** domiciliada en Cleveland, Ohio, Estados Unidos de América y solicitante de la patente de invención citada en referencia, muy respetuosamente me permito manifestar a su despacho que **SUSTITUYO** el poder a mi conferido por la mencionada sociedad al Doctor **HUMBERTO RUBIO CAMACHO,** mayor de edad, identificado con la cédula de ciudadanía No. 17.192.062 de Bogotá, Abogado en ejercicio portador de la Tarjeta Profesional No. 50007 del Consejo Superior de la Judicatura, domiciliado en la Carrera 7 No. 74-64, Oficina 506 de Bogotá, D.C., Colombia, **con las mismas facultades que me fueron otorgadas**.

Por lo tanto de manera atenta solicito a ésa Dependencia, se sirva reconocer la personería respectiva al Doctor **HUMBERTO RUBIO CAMACHO** en su calidad de apoderado de la sociedad **PPG INDUSTRIES OHIO, INC.**, dentro del presente proceso.

Atentamente,

**MARCELA GOMEZ RUBIO**
**C.C. 52.886.586 de Bogotá**
**T.P. 137950 del Consejo Superior**
**De la Judicatura.**

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Santafé de Bogotá, 27 JUL. 2008
Presentado personalmente por Marcela
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T. 137950
Suscrito
NOTIFICADOR

Acepto

**HUMBERTO RUBIO CAMACHO**
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**COD 4134**

*07/2300/P000645/Mgr.-*

Industria y Comercio
SUPERINTENDENCIA

**DIVISIÓN DE NUEVAS CREACIONES**

RADICACIÓN EXPEDIENTE No. 07-39467

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCIÓN**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **587** DE

FECHA **18 DE ENERO DE 2008** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **16 DE ABRIL DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ NO ____X____

# United States Patent [19]

**Ruetman et al.**

[11] **Patent Number: 4,920,167**

[45] **Date of Patent: Apr. 24, 1990**


[54] **ANTISTATIC POLYURETHANE-UREA DISPERSIONS**


[75] Inventors: **Sven H. Ruetman**, Walnut Creek; **Joginder N. Anand**, Clayton; **G. Robert Collins**, Walnut Creek, all of Calif.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.



[21] Appl. No.: **269,506**

[22] Filed: **Nov. 10, 1988**

[51] **Int. Cl.**[5] ..... **C08G 18/06**

[52] **U.S. Cl.** ..... **524/155**; 524/165; 524/174; 524/183; 524/184; 524/280; 524/361; 524/364; 524/376; 524/377; 524/392; 524/394; 524/404; 524/406; 524/408; 524/413; 524/414; 524/418; 524/421; 524/423; 524/424; 524/429; 524/434; 524/435; 524/436; 524/437; 524/438; 524/590; 524/591

[58] **Field of Search** ..... 524/591, 839, 184, 404, 524/421, 701, 746, 361, 364, 590, 376, 377, 770, 761, 762, 706, 723, 729, 742, 745, 773, 779, 796, 155-174, 183, 280, 392, 394



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[57] **ABSTRACT**

Disclosed is dispersion of a polyurethane-urea polymer in a continuous phase. This dispersion contains about 0.1 to about 5 parts by weight of an ionizable, non-volatile salt per 100 parts by weight of polyurethane-urea polymer. Polyurethane-urea coatings made from this dispersion have excellent static dissipative properties.


**17 Claims, No Drawings**

more preferably less than 0.5 second, and most preferably less than 0.25 second.

In addition to the foregoing components, additives such as colorants, antioxidants, UV stabilizers, fillers, flame retardants, preservatives, surfactants, adhesion promoters and the like may be used, if desired.

The dispersion of this invention is useful in preparing static dissipative coatings, films, membranes and the like. Such as readily prepared in known manner for the dispersion of this invention by applying same to a convenient substrate and removing the continuous phase. Subsequent curing is not normally necessary, although it may be desirable to subject the polymer to an elevated temperature in order to drive off residual amounts of the continuous phase. Suitable techniques for preparing films and coating are described in copending application Ser. No. 200,287, filed May 31, 1988, incorporated by reference. Typical films, membranes and coatings have a thickness from about 0.1 to about 50 mils.

The dispersion of this invention is of particular interest in providing static dissipative coatings for a variety of substrates, of which electronic packaging is of particular importance. Other important uses include in preparing antistatic coatings for conveyor and drive belts, coatings for flammable materials packaging and handling devices, preparing antistatic footwear, coatings for materials used in dust-free environments, and the like. Antistatic lacquers and printing aids are another important use of this invention.

An especially important use of this dispersion is in preparing static dissipative coatings for thermoplastic films The coated films are useful in making wrappings, bags and other packaging materials for electronics components. The coated films can also contain a metal layer to further improve its conductivity.

## ILLUSTRATIVE EMBODIMENTS

The following examples are provided to illustrate the invention and are not intended to limit the scope thereof. Unless stated otherwise, all parts and percentages are given by weight.

### EXAMPLE 1

In a suitable vessel are added 6.8 parts of 2,2-bis(hydroxymethyl)-propionic acid, 100 parts of a 2000 molecular weight, nominally difunctional ethylene oxide-capped poly(propylene oxide) and 40 parts of $H_{12}$-methylene diphenyldiisocyanate ($H_{12}$MDI). This mixture is stirred under a nitrogen atmosphere at 100° C. for two hours. It is then cooled to 70° C. and 0.47 parts of octadecyl-3,5-di-t-butyl-4-hydroxyhydrocinnamate (a stabilizer) is added. After about five minutes stirring, 1.6 parts of sodium tetraphenyl boron is added. After another five minutes stirring, 4.9 parts triethylamine is added and the stirring continued for additional 20 minutes at 70° C., after which time an opaque, viscous resin is obtained. With rapid agitation, 350 parts of water are added to form a dispersion, and then a solution of 3 parts of ethylenediamine in 50 parts of water is added with rapid agitation. An additional 50 parts of water is used to rinse the ethylenediamine container and is added to the dispersion. The resulting dispersion is stirred for 60 minutes at ambient temperate. It has a pH of 9 and contains 25.4% solids by weight. This dispersion is referred to as Sample No. 1.

Dispersion Sample No. 2 is made in the same manner, except the sodium tetraphenyl boron is added after the ethylenediamine is added and permitted to react.

Comparative Sample A is prepared in the same manner as Example No. 1, except the sodium tetraphenylboron is omitted.

Films are prepared from emulsion Samples Nos. 1 and 2 and Comparative Sample A by pouring the dispersions into 8×21 cm molds and permitting them to dry for 24 hours at ambient conditions. The resulting transparent strips are demolded and hung in a fume hood for an additional 48 hours. At this point the films are about 0.06 cm thick.

The resulting films are evaluated for surface resistivity and static dissipative properties. Before testing, they are conditioned for 90 hours at 12% relative humidity. Surface resistivity is measured by ASTM D-257. The results are as indicated in Table 1 following.

TABLE 1

| Sample No. | Wt. −% Salt [1] | Decay Time [2], sec. | Surface Resistivity, ohms/sq |
|---|---|---|---|
| A* | 0 | 5.24 | $9.5 \times 10^{12}$ |
| 1 | 1 | 0.02 | $1.1 \times 10^{11}$ |
| 2 | 1 | 0.02 | $4.5 \times 10^{10}$ |

*Not an example of this invention.
[1] Based on weight of polymer.
[2] Time required to dissipate 99% of an applied charge of 5000 VDC.

As illustrated by the data in Table 1, the addition of only 1 weight percent salt decreases the static decay time to essentially zero. This demonstrates the unusual effectiveness of the salt in polyurethane-urea formulations. Also of note are the reductions in resistivity, which approximate two orders of magnitude.

### EXAMPLE 2

Samples No. 1 and 2 are repeated, substituting in each instance an equal quantity of sodium trifluoromethylsulfonate for the sodium tetraphenyl boron. When the sodium trifluoromethylsulfonate is added to the prepolymer, the resulting film exhibits a static decay time of 0.08 seconds and a surface resistivity of $8.9 \times 10^{11}$ ohms/square. When the sodium trifluoromethylsulfonate is added to the prepolymer, the resulting film exhibits a static decay time of 0.11 seconds and also has a surface resistivity of $8.9 \times 10^{11}$ ohms/square.

### EXAMPLE 3

A coated substrate is prepared by coagulating a thin film of an static dissipative polyurethane-urea polymer on a polystyrene film. The polyurethane-urea polymer is prepared in the same manner as Sample No. 1, except it contains 1% by weight sodium trifluoromethylsulfonate in place of sodium tetraphenyl boron. The uncoated polystyrene film has essentially no static dissipative properties. However, the coated substrate dissipates 90% of an applied +5000 volt charge in 1.08 seconds, and 90% of an applied −5000 volt charge in 1.22 seconds. At 50% relative humidity, the coated sample is three orders of magnitude lower in surface resistivity.

What is claimed is:

1. A dispersion of a polyurethane-urea polymer in a continuous aqueous phase, said dispersion containing about 0.1 to about 5 parts by weight of an alkali metal or alkaline earth metal salt of a thiocyanate ion, fluorinated alkyl sulfonate ion or tetraorganoboron ion per 100 parts by weight of polyurethane-urea polymer.

2. The dispersion of claim 1, wherein the polyurethane-urea polymer is a neutralized reaction product of

a reaction mixture comprising a polyamine curing agent and an isocyanate-terminated prepolymer.

3. The dispersion of claim 2, wherein said prepolymer is the reaction product of a polyisocyanate, a polyether polyol and a polyol containing an ionic or potentially ionic group.

4. The dispersion of claim 3 wherein said prepolymer contains about 10 to about 150 milliequivalent of ionic groups/100 grams, and said polyol containing an ionic or potentially ionic group is a dihydroxy alkanoic acid.

5. The dispersion of claim 4 wherein the continuous phase is aqueous.

6. The dispersion of claim 1 wherein the salt is a tetraphenyl boron salt or a fluorinated alkyl sulfonate salt.

7. The dispersion of claim 4 wherein the salt is a tetraphenyl boron salt or a fluorinated alkyl sulfonate salt.

8. The dispersion of claim 5 wherein the salt is a tetraphenyl boron salt or a fluorinated alkyl sulfonate salt.

9. The dispersion of claim 2, wherein said prepolymer is the reaction product of a polyisocyanate, a polyester polyol and a polyol containing an ionic or potentially ionic group.

10. A substrate having a static dissipative coating comprising a polyurethane-urea polymer having dispersed therein from about 0.1 to about 5 parts, per 100 parts by weight polymer, of an alkali metal or alkaline earth metal salt of a thiocyanate ion, fluorinated alkyl sulfonate ion or tetraorganoboron ion.

11. The substrate of claim 10 wherein the salt is a tetraphenyl boron salt or a fluorinated alkyl sulfonate salt.

12. The substrate of claim 10 wherein the polyurethane-urea polymer is a neutralized reaction product of a reaction mixture comprising a polyamine curing agent and an isocyanate-terminated prepolymer.

13. The substrate of claim 12 wherein said prepolymer is the reaction product of a polyisocyanate, a polyether polyol and a polyol containing an ionic or potentially ionic group.

14. The substrate of claim 13 wherein said prepolymer contains about 10 to about 150 milliequivalents of ionic groups/100 gram, and said polyol containing an ionic or potentially ionic group is a dihydroxy alkanoic acid.

15. The substrate of claim 12 wherein said prepolymer is the reaction product of a polyisocyanate, a polyester polyol and a polyol containing an ionic or potentially ionic group.

16. A static dissipative polyurethane-urea polymer prepared by coagulating the dispersion of claim 1.

17. A static dissipative polyurethane-urea polymer prepared by coagulating the dispersion of claim 4.

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