Liquid composition to generate a removable temporary protection film, based on aqueous dispersions of polyurethane
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LIQUID COMPOSITION TO GENERATE A REMOVABLE TEMPORARY PROTECTION FILM, BASED ON AQUEOUS DISPERSIONS OF POLYURETHANE

BACKGROUND

The protection of metallic, plastic or glass pieces has been accomplished by the use of adhesive impregnated polyolefin films that allow them to attach to various substrates.

Though these adhesive impregnated films have had several convenient features, such as their low cost, they have some issues, like the fact that they are not fully adaptable to all surfaces, in other words, they do not always mold exactly to the contours and fanciful shapes of the pieces. Furthermore, the adhesive can show degradation problems or even transfer to the substrate, which could result in damage to the coated surface, or induce flaws on it, such as the spots called "ghosts". Further, the fact that they do not mold exactly to the surface of the pieces can result in some moisture infiltration that might eventually affect the surface of the substrate by oxidation, for example. In addition to the above mentioned shortcomings, is the fact that the labor required for the application of the adhesive films can be sometimes quite intensive.

One way to solve these disadvantages is to apply a liquid composition, capable of generating a film once it is dry. Said film must be easily removable and must have, among other features, sufficient resistance to certain chemical substances and scratches, and should be able to mold to the shape and features of the surfaces to be covered with it, insomuch that avoids the infiltration of moisture to the surface of the substrate.

Regarding this concept, several works have been done, such as WO 2004/85082, which describes the manufacture of a protecting removable layer from a liquid substance, which is basically an acrylic copolymer. The mentioned publication also describes the application method, which is by spraying. The use of the above said copolymer in mixture with aqueous dispersions of polyurethane is not mentioned.

WO 2004/46228 describes the use of a polyisoprene-based, or its by-products, liquid composition. In this case, the mentioned liquid composition does not consider the use of polyurethane dispersions as those used in the present disclosure, nor the use of release agent such as is described in present disclosure. Protection of surfaces in motorized vehicles, such as automobiles, trucks and motorcycles is described.
The use of natural materials, such as polysaccharides or its derivatives, as well as polymeric composites, such as the polyamines, is described within WO 2002/79332. Such composites are dissolved in aqueous solutions, and are used for a temporary protection of substrates, like a vehicle. The solutions are capable of providing films that can be resistant to water, and that are not toxic.

WO 2002/24346 describes the use of an emulsion of vinyl-acrylic copolymer with ethylene-vinyl acetate and a plasticizer. The use of any dispersion of polyurethane or either mixtures of this with any other kind of polymeric material is not described in such publication.

WO 2002/24346 describes a composition of aliphatic polyester, or partially aromatic polyester, polyester-urethane, or polyester-amide, or polyester-carbonate along with filler having a particle size, which must not be larger than 10 micrometers. Such composition is intended to protect plastic materials, glass or paint coated surfaces. Such a composition is placed in a non-aqueous dilution, which differs from the present disclosure.

The use of solutions of elastomers has also been disclosed. For example, in U.S. 6,1 10,525, where it describes the use of butadiene homopolymer latex or copolymers of this with styrene or copolymers of ethylene-vinyl acetate. Such compositions are used for the protection of automotive surfaces. The use of mixtures of the mentioned components with emulsions of polyolefin and/or polyurethane dispersions is not described.

U.S. 6,124,044 describes the use of aqueous emulsions of vinyl-acrylic copolymer and ethylene-vinyl acetate emulsions in order to form films, which might be able to be removed from the surfaces they have been applied on. The use of the above mentioned materials with mixtures of aqueous dispersions of polyurethane, or with emulsions of some butadiene-based elastomer, is not mentioned.

Liquid compositions which provide films that are removable by mechanical action (manually) or peeling off; or by the use of alkaline solutions or slightly acid solutions; or using pressurized water or hot water are described in U.S. 5,801,174; 5,639,814; and 6,187,849.

U.S. 5,945,462 describes the use of aqueous solutions that have pre-polymers of urethane with acrylic functionalities, susceptible to polymerization by a photoinitiator, when it is irradiated with ultra-violet light. The resulting product of this photo-polymerization is a removable film with a protective usage. The utilized release agents, in
other words, the additives that help the film to be removed more easily are polyethylene glycols, fatty acids and lecithin.

U.S. 2004/0009354 A1 describes the use of aqueous dispersions of polyurethane along with release agents, particularly glycerol, and a dispersion of metallic salts of stearic acid, or a dispersion of a wax. Such a liquid mixture is capable of providing a film able to protect plastic, metal and glass materials. The polyurethane component may be a polyurethane-urea and/or sulpho poly(ester-urethane) that can optionally contain silyl groups. The use of polyurethane based on a polycarbonate or mixtures of polyurethane with butadiene based elastomeric emulsions is not mentioned. Furthermore, the use of release agents such as a mixture of polyolefin/poly(tetrafluoroethylene) is not mentioned.

**SUMMARY**

In one aspect, the present disclosure provides a liquid composition capable of providing a film that may be used for a temporary coating with the function of protecting polymeric materials, such as acrylic, polycarbonate, polystyrene, polyester, acrylonitrile-butadiene-styrene terpolymers, polyurethanes, amongst others. Likewise, in order to temporarily protect glass, ceramic materials, and metal materials such as carbon steel, stainless steel, as well as aluminum. The intention of protecting these materials is during their handling, their transportation or their exposure to chemical products, such as automotive paint substances. For example, one proposed application is to use the product like a temporary masking film when a car is repaired and to be painted.

In another aspect, the present disclosure provides a liquid composition that provides a film as a temporary protective coating which can be flexible enough to avoid presenting fractures or cracking.

In yet another aspect, the present disclosure provides a liquid composition that can be applied by the use of spraying processes, or even by means of a brush or roller, or by immersion processes, and which is capable of providing a film as a temporary protective coating, capable of resisting chemical or mechanical threats, and which is easily removable from the substrate it has been applied to.

In another aspect, the present disclosure provides a liquid composition that can provide a film for temporary protection, that, when removed from the substrate it has been
applied to, does not modify the appearance of the substrate, and does not exhibit any transference of the coating to the protected surface.

In another aspect, the present disclosure provides a liquid composition that can provide a film for temporary protection, which is capable of resisting chemical substances, such as isopropyl alcohol, turpentine oil and that will be waterproof once it has been well dried.

**BRIEF DESCRIPTION OF THE DRAWING**

Fig. 1 is a depiction of a thermogram for the protective film of Example 2.

**DETAILED DESCRIPTION**

In one aspect, the present disclosure provides a liquid composition that can be applied either by spraying, atomization, brush, roller or immersion, among other conventional coating methods. Once the liquid composition has been applied and dried, a film will result, which can temporarily protect the substrate it has been applied to, and is chemically and mechanically resistant, and will be flexible enough to be easily removed from the substrate it protects, without presenting any transfer to the substrate.

This removability is one of the convenient features of the temporary protection film that is provided, for it can be removed in one piece or in large portions and it simplifies the film removal task. Another convenient feature of the temporary protection film, provided from this liquid composition, is its resistance to substances such as some alcohols, oils and greases.

Another remarkable feature of the liquid composition obtained in some aspects of the present disclosure is the generation of films for the temporary protection of various materials, such as metal, plastic, glass and ceramic.

The liquid composition of the present disclosure is comprised of an aqueous dispersion of aliphatic and carboxyl functionalized polyurethane, which can be based on polyester, polyether, or even a structure with units of polycarbonate, that bestow chemical and mechanical resistance features to the film that will be provided through the drying process.

The desirably used polyurethanes are aliphatic polyurethanes and/or co-polymers of aliphatic/ acrylic polyurethane. The preparation of water dispersed polyurethanes containing functional groups, such as carboxyl for instance, is documented and reported in

A dispersion is defined as an immiscible mixture of one component in another, specifically of a solid in a liquid. In this case, a dispersion of polyurethane refers to a mixture of polyurethane in water.

The polyurethane content of the aqueous dispersion of the liquid composition of the present disclosure is employed in the range of 50 to 100 % by weight, in other embodiments from 60 to 90 % by weight, and from 15 to 85 % by weight based on the total weight of the liquid composition.

The aqueous dispersion of polyurethane may comprise one type of polyurethane, for example, aliphatic or mixtures of various "soft" polyurethanes, and "hard" polyurethanes; in such cases, the soft polyurethanes may be rather utilized in a higher proportion, since their elongation is greater than that of the hard polyurethanes. The commonly used proportions of soft polyurethane to the hard polyurethane are in a weight ratio from 4 to 9. In other words, for each 4 to 9 grams of soft polyurethane there is 1 gram of hard polyurethane. The preceding will depend on the stiffness features that are desired in the film generated from the liquid composition.

As mentioned above, the liquid composition may be comprised of an aliphatic and functionalized polyurethane dispersion, or a mixture of such a polyurethane with other polymers, especially those which provide mechanical resistance features, and those that can provide the resulting film with elastomeric and easy removal features.

With regard to suitable polymeric materials with elastomeric capabilities, those with a molecular weight over 50,000 g/mol are preferable, more preferable are those with a molecular weight less than 450,000 g/mol, and most preferable are those whose molecular weight does not exceed the 250,000 g/mol. It is more desirable that those elastomeric polymers have, within their structure, functional groups that are capable of chemically interacting with either with the polyurethane based dispersion, or with any cross-linking agent that might be added to the liquid composition in order to improve the chemical and mechanical resistance properties of the film that may be provided from this.
A suitable elastomeric polymer may be selected from, but is not limited to, a random styrene-butadiene copolymer aqueous dispersion, or latex, functionalized with carboxyl groups. The molecular weight of such material is greater than 20,000 g/mol. In this case, the content of the liquid composition for the present invention is from between 2 and 20% by weight, in other embodiments from 4 to 17% by weight, and from 5 to 15% by weight based on the total weight of the liquid composition.

Another example of a suitable elastomeric polymer is the butadiene homopolymer with functional groups along its main chain, though it is more desirable for those groups to be located at the ends of the polymeric chains.

Another component of the liquid composition of the present disclosure is a release agent whose main function is to ease the removal of the protective film, once the liquid composition has been applied and dried. Furthermore, in the present disclosure, such release agents, given their physical-chemical features, are also capable of imparting some mechanical and chemical resistance to the protective film that is provided from the liquid composition of the present disclosure, as well as to modify the flexibility of such film. Some examples of suitable release agents include, but are not limited to, pentaerythritol, glycerin, oxidized polyethylene based waxes dispersed in water, poly(tetrafluoroethylene), mixtures of polyethylene and poly(tetrafluoroethylene), diglycerol, triglycerol, polyethylene glycol, ethers and esters of ethylene glycol, beaver oil, ethoxylated or non ethoxylated polydimethylsiloxanes. Preferred release agents include oxidized polyethylene waxes dispersed in water, glycerin, polyethylene glycol, poly(tetrafluoroethylene), as well as the mixtures of polyethylene with poly(tetrafluoroethylene); and combinations thereof.

The content of the release agent, alone or in any combination, in the liquid composition of the present disclosure, is generally from 0.2 to 50% by weight, from 0.5 to 30% by weight, or from 1 to 20% by weight based on the total weight of the liquid composition.

Another component of the liquid composition of the present disclosure is a cross-linking agent. The cross-linking agent is a compound capable of reacting with the functional groups from the polyurethane or other components having functional groups, to generate a protective film having desirable chemical and mechanical resistance. Examples of suitable cross-linking agents include, but are not limited to, melamines, aziridines,
epoxysilanes, carbodiimides, or polyurethanes. In the case of the present disclosure, it is preferred to use polyaziridine and methyl glycidosypropyl diethoxy silane. The content of the cross-linking agent in the formulation of the liquid composition of the present invention ranges from 1 to 10 % by weight, from 2 to 7 % by weight, or from 3 to 5 % by weight, based on the solids content of the polyurethane dispersion and solids content of any other component with functional groups.

Due to the fact that the polymeric materials are generally degraded when exposed to open-air, by the effect of ultraviolet light and/or ozone, it is desirable to add ultraviolet light stabilizers, since such additives can provide a significant reduction, or even the elimination of, the yellowing in the protective film coating. Some examples of such stabilizers are: the mixture of bis-(1,2,2,6,6-pentamethyl-4-piperydyl) sebace, methyl-(1,2,2,6,6-pentamethyl-4-piperidyl) sebace, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylthyl)-4-hydroxybenzene propanoic acid, C7-C9-branched alkyl esters, and dimethyl sebace. The amounts of stabilizer utilized in the liquid composition of the present invention range from 0.2 to 7 % by weight, from 0.2 to 5 % by weight, or from 0.5 to 3 % by weight, based on the total solids in the liquid composition of the disclosure.

Another component in the liquid composition of the present disclosure is a rheology modifying agent, known as a thickening agent, whose main function is to prevent, or minimize, dripping of the material when it is applied, as well as to obtain thicker films. The amount of this additive in the liquid composition ranges from 0.01 % to 1 % by weight, from 0.03 to 0.5 % by weight, or from 0.05 to 0.2 % by weight, based on the total weight of the liquid composition.

Another component of the liquid composition of the present disclosure is the filler. Filler materials accomplish the task of reducing costs, but even more important, is the fact that they impart various mechanical features to the protective film. Especially, the use of fillers improves the protective film's resistance to scratching, and reduces the drying time, which can be quite important for some applications.

There are many sorts of filler materials, such as calcium carbonate, talc, glass microspheres, polymeric microspheres, or cristobalite. In the present disclosure, the use of polymeric microspheres, made from acrylic materials; or talc, is preferred, given the amounts of these materials that can be incorporated to the liquid composition, considering also that they reduce the drying time of the liquid composition once it has been applied.
The liquid composition of the present disclosure is not limited to the components described thus far. Other additives which may be incorporated include, but are not limited to, moisturizing agents, coalescent agents, dispersant agents that might take part on the formulation of the liquid composition of the present disclosure, as known to those skilled in the field.

Once the liquid composition of the present disclosure is formulated, it may be applied by various means well known to those skilled in the art, including, but not limited to, spraying, brushing, or a rolling onto the material to be coated and protected.

The thicknesses of the temporary protective film provided through the application of the liquid composition onto the material to be protected, such as by means of a spraying process, are selected in such way that they allow the temporarily protective film to be easily removed from the coated material. For example, for most of the surfaces to be protected such as those of metallic, plastic, glass, wood and ceramic materials, a minimum thickness of 0.002 inches (51 micrometers) must be achieved. Otherwise, removal of the provided film is difficult and not in possible large portions, or even in a single piece. Also, as the thickness increases the peel force increases, and the ease of removal decreases, especially above 0.006 inches (152 micrometers). Therefore, due to the tradeoff between thickness and ease of removal, the preferred thickness range is from 0.002 to 0.006 inches (51 to 152 micrometers).

Next, some examples of formulations for the liquid composition, as well as some applications according to the disclosure are listed. Such examples are not limited, in terms of formulation of the liquid composition and of the application method, as it will appear obvious to any skilled person in the field. Regarding the expected performance of the generated film, it can be pointed out that it must be resistant to paint and its solvent, with a tack free drying time no more than 30 minutes, usually with a tack free drying time from 2 to 20 minutes. Further, the film will exhibit a peel force between 3 to 800 g/in, when measured at a crosshead speed of 30 cm/min and with a minimum elongation at break of 10 % and minimum tensile strength of 2.5 MPa. Also, depending upon application the film can be transparent or not.
Example 1

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

1000 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206 from Stahl de Mexico, Toluca, Edo. De Mex., Mexico); 3 % by weight (9.9 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100, a polyaziridine, available from DSM Neoresins, Waalkwijk, Netherlands); 3 % by weight (9.9 grams), based on the total solids content, of ultraviolet stabilizer (TINUVIN 5050 from Ciba Specialties Chemicals Co., Tarrytown, NY, USA); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30 from Ciba Specialties Chemicals Co., Tarrytown, NY, USA).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition had a milky appearance. This liquid composition was applied to a glass plate measuring 10 centimeters (cm) wide, 30 centimeters (cm) long and 3 millimeters (mm) thick; using a conventional spraying system (Spray gun from Binks, Glendale Heights IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature, 22-26 °C, a protective film was obtained. This film was difficult to peel off in one piece, by hand, it was removed in three pieces.

Example 2

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

800 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 200 grams of wax (a 31 % solids emulsion of oxidized polyethylene, 474N30, provided by Ceras Universales SA de CV, DF, Mexico); 3 % by weight (7.92 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9.78 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TINUVIN 5050); and 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of a rheological modifier (VISCALEX VH30).
All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition had a milky aspect. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature, 22-26 °C, a protective film was obtained. This film was more easily peeled off, by hand, than the film from Example 1, and in one piece also, but it exhibited a greater stiffness.

**Example 3**

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

- 980 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 3 % by weight (9.7 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9.7 grams), based on the solid content of polyurethane dispersion, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 20 grams of a mixture of polyethylene/poly(tetrafluoroethylene) as release agent (AQUAPOLYFLUO 411 from Micro Powders, Inc., Tarrytown, NY, USA).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition had a milky aspect. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm. After drying, for 24 hours at room temperature, 22-26 °C, a protective film was obtained. This film was more easily peeled off in one piece, by hand, than the films from Examples 1 and 2.

**Example 4**

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:
960 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 3 % by weight (9.5 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9.5 grams), based on the solids content of polyurethane dispersion, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) as release agent (AQUAPOLYFLUO 411).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying, for 24 hours at room temperature, 22-26 °C, a protective film was obtained. This film was more easily peeled off in one piece, by hand, than the films from Examples 1, 2, and 3.

The liquid compositions from Examples 1, 2, 3, and 4 were also applied to automotive paint coated metallic plaques, measuring: 10 cm wide, 30 cm long and 2 mm thick, and dried at room temperature (22-26 °C) for 1 hour, then heated in a 60 °C oven for 3 minutes, and then allowed to cool and equilibrate for 48 hours at room temperature, 22-26 °C. Next, the peel strength of the resulting protective films was evaluated, at an angle of 180° on samples having a width of 2.54 cm and a length of 30 cm, using a Universal Electromechanical Testing Machine (Model 5564 from Instron, Norwood, MA, USA) with the crosshead speed set at 30 cm/min, and a test length of 5 cm. Therefore, it was possible to obtain 4 measurements from the same metallic plaque. The reported values are the average of four measurements. In Table 1, the results from this evaluation can be seen. The main difference between the liquid compositions 1, 3 and 4 is the presence of the polyethylene/poly(tetrafluoroethylene) release agent in Examples 3 and 4; while in the liquid composition from Example 2 the release agent employed was the oxidized polyethylene wax.
Table 1. Peel strength, Examples from 1-4

<table>
<thead>
<tr>
<th>Examples</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Release Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.071</td>
<td>403.4</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>0.076</td>
<td>260.4</td>
<td>Wax (20 % w/w)¹</td>
</tr>
<tr>
<td>3</td>
<td>0.077</td>
<td>189.9</td>
<td>PE/PTFE (2 % w/w)¹</td>
</tr>
<tr>
<td>4</td>
<td>0.073</td>
<td>106.3</td>
<td>PE/PTFE (4 % w/w)¹</td>
</tr>
</tbody>
</table>

¹ w/w equal to percentage by weight

As can be seen from Table I, addition of the oxidized polyethylene wax reduces the peel strength required to remove the protective film off the metal plaque. When a polyethylene/poly(tetrafluoroethylene) mixture is used as a release agent, it results in a significant decrease in the strength that is required to peel the film off the metallic plaque. When the amount of the polyethylene/poly(tetrafluoroethylene) mixture is doubled, there is a further decrease in the peel strength in the protective film.

In the following examples, the use of other release agents is shown.

**Example 5**

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

910 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of glycerin provided by Sigma Aldrich, Toluca, Mexico; 3 % by weight (9 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9 grams), based on the solids content of polyurethane dispersion, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411).

At the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C),
a protective film was obtained. This film was easily removed. This film also exhibited a
greater flexibility than the films from the previous Examples 1 - 4. Flexibility was
evaluated in a subjective manner, as it was stretched and bent by hand.

Example 6

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room
temperature (22-26 °C) with the following composition:

910 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and
carboxyl functionalized polyurethane (RU-41206); 50 grams of polyethylene glycol
(PLURACOL E-400 from Poliøles, Lerma, Edo. de Mex., Mexico); 3 % by weight (9
grams), based on the solids content of polyurethane dispersion, of cross-linking agent
(CX-100); 3 % by weight (9 grams), based on the solids content of polyurethane
dispersion, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based
on the total weight of the liquid composition of rheological modifier (VISCALEX VH30);
40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO
411).

All the components were mixed for 60 minutes using a high torque stirrer having a
3 bladed type propeller. The resulting liquid composition was applied to a glass plate
measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system
(Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE
needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 0C),
a protective film was obtained. This film was easily peeled off, in one piece, and with
greater flexibility than the films obtained in Examples 1 - 4, but less flexibility than the
film from Example 5. This is a result of using a component, polyethylene glycol, with a
greater molecular weight, which results in a less plasticized film compared to Example 5.

Example 7

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room
temperature (22-26 0C) with the following composition:

860 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and
carboxyl functionalized polyurethane; 50 grams of wax (474N30); 50 grams of
polyethylene glycol (PLURACOL E-400); 3 % by weight (8.51 grams), based on the
solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (8.98 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was more easily removed than the films obtained in the Examples 1 - 6. As for flexibility, the film of this example was less flexible than those from Examples 5 and 6, due to the presence of the wax (emulsion of oxidized polyethylene) in this example. The resistance to scratching of this film was observed to be greater than that of the films from Examples 1, 3, 4, 5, and 6 but less than that of the film of Example 2, where 20 % w/w of wax was added. This result indicated that the wax (emulsion of oxidized polyethylene) imparts not only peeling ease to the film, but some scratch resistance as well.

The liquid compositions from Examples 4, 5, 6, and 7 were applied to automotive paint coated metallic plaques, measuring 10 cm wide, 30 cm long and 2 mm thick; and dried at room temperature (22-26 °C) for 1 hour, then heated in a 60 °C oven for 3 minutes, and then allowed to cool and equilibrate for 48 hours at room temperature, 22-26 °C. Next, the peel strength of the resulting protective films was evaluated, at an angle of 180° on samples having a width of 2.54 cm and a length of 30 cm, using a Universal Electromechanical Testing Machine (Model 5564 from Instron, Norwood, MA, USA) with the crosshead speed set at 30 cm/min, over a distance of 5 cm. Therefore, it was possible to obtain four measurements from the same metallic plaque. The reported values are the average of four such measurements. In Table 2, the results from this evaluation can be seen.
Table 2. Peel strength, Examples 1, 2 and from 4 - 7

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Release Agent</th>
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<tr>
<td>1</td>
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<td>Wax (20 % w/w)</td>
</tr>
<tr>
<td>4</td>
<td>0.073</td>
<td>106.3</td>
<td>PE/PTFE (4 % w/w)</td>
</tr>
<tr>
<td>5</td>
<td>0.074</td>
<td>280</td>
<td>PE/PTFE (4 % w/w) + Glycerin (5 % w/w)</td>
</tr>
<tr>
<td>6</td>
<td>0.071</td>
<td>27.1</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)</td>
</tr>
<tr>
<td>7</td>
<td>0.072</td>
<td>102.5</td>
<td>PE/PTFE (4 % w/w) + Wax (5 % w/w) + PEG (5 % w/w)</td>
</tr>
</tbody>
</table>

From the information shown in Table 2, it can be seen that the combination of polyethylene glycol with the mixture of polyethylene/poly(tetrafluoroethylene) (as shown in Example 6) brings a significant decrease in the peel strength when compared to the one obtained when not using any release agent (Example 1).

Further, when polyethylene glycol is added to a mixture that contains wax (emulsion of oxidized polyethylene), as in Example 7, there is a significant decrease in the peel strength (compared to Example 2) required to remove the protective film, which indicates that the polyethylene glycol acts as a very effective release agent.

On the other hand, the presence of glycerin increases the peel strength (see Example 5 versus Example 4), probably due to the plasticizing effect of such an additive to the protective film, which brings on a more flexible and less thick film, because viscosity of the sprayable mixture is reduced. However, the peel strength of Example 5 is still less than that of the film obtained with no release agent at all (Example 1).

In the following examples, the use of two different types of filler is stated, particularly the polymeric micro sphere, and the talc.

Example 8

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:
843 grams of a 33 % aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 3 % by weight (8.35 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (8.81 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (f INUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of a protective film (AQUAPOLYFLUO 411); 50 grams of polyethylene glycol (PLURACOL E-400); and 17 grams of filler, specifically polymeric microspheres (MS) (EXPANCEL 461 WET 20d36 with a particle size from 20 to 30 micrometers and density of 36 +/- 3 kg/m³ from Expancel, Stockviksverken, Sweden).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was easily removed, by hand, and observed to be slightly less flexible than the films obtained in the previous Examples 1 - 7. As for the resistance to scratching of this film, it had the same performance as those from the preceding examples. On the other hand, the drying time decreased with respect to the preceding examples, since this film was dry to the touch in just 12 minutes.

**Example 9**

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

760 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 3 % by weight (7.52 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (7.99 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of
polyethylene/polytetrafluoroethylene) (AQUAPOL YFLUO 411); 50 grams of polyethylene glycol (PLURACOL E-400); and 100 grams of filler, specifically talc (YELLOWSTONE 325 provided by Luzenac Sierra SA de CV, Ecatepec, Edo. de Mex., Mexico).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was easily removed, by hand, and observed to be less flexible than the films obtained in the previous Examples 1-8. As for the resistance to scratching, it had a better performance than the ones from the preceding examples. Further, the drying time was considerably shortened, since this film was dry to the touch in just 5 minutes.

The liquid compositions from Examples 1, 7, 8, and 9 were applied to automotive paint coated metallic plaques measuring 10 cm wide, 30 cm long, and 2 mm thick; and dried at room temperature (22-26 °C) until they could be touched without leaving any fingerprints on the surface of the protective film. This time was recorded. Later, they were heated in a 60 °C oven for 3 minutes, then cooled and equilibrated for 48 hours at room temperature, 22-26 °C. Next, the peel strength of the protective films was evaluated, at an angle of 180° on samples having a width of 2.54 cm and a length of 30 cm, using a Universal Electromechanical Testing Machine (Model 5564 by Instron, Norwood, MA, USA) with the crosshead speed set at 30 cm/min, over a distance of 5 centimeters. Therefore, it was possible obtain 4 measurements from the same metallic plaque. The reported values are the average of four such measurements. In Table 3 the results from this evaluation, as well as the dry to the touch times are reported.

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Dry to touch time, min</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.071</td>
<td>403.4</td>
<td>30</td>
<td>None / None</td>
</tr>
<tr>
<td>7</td>
<td>0.072</td>
<td>102.5</td>
<td>20</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w) + Wax (5 % w/w) / None</td>
</tr>
</tbody>
</table>
As shown in Table 3, the peel strength required to remove the protective film, when adding polymeric microspheres (Example 8), is similar to a material without filler (Example 7). Whereas when the added element was talc (Example 9), the peel strength was increased by 36 g/in.

In other words, the film is slightly less easy to remove. As for the drying time, there is a considerable improvement when some filler was added, particularly with talc (Examples 7 vs. Examples 8 and 9).

The presence of fillers (Examples 8 and 9) results in a faster drying of the liquid composition, and the peeling ease is greater when compared to the peeling ease of a film without any release agents (Example 1).

Further, the mechanical features of the protective film containing a filler were modified, resulting in stiffer films. In Table 4, the values for tensile strength and elongation at break for the films from Examples 1, 7, 8, and 9, are shown.

Measurements were made on four 2.5 cm wide and 10 cm long film specimens using a Universal Electromechanical Testing Machine (Model 5564 from Instron, Norwood, MA, USA) following the established protocol described in the Test Method ASTM D-882 (2002). The reported values are the average of four such measurements.

Table 3. Mechanical features of the protective film

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Dry to touch time, min</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.082</td>
<td>99</td>
<td>12</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)+ Wax (5 % w/w) / MS (1.7 % w/w)</td>
</tr>
<tr>
<td>9</td>
<td>0.077</td>
<td>139.1</td>
<td>5</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)+ Wax (5 % w/w) / Talc (10 % w/w)</td>
</tr>
</tbody>
</table>

Table 4. Mechanical features of the films of Examples 1, 7, 8, and 9

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.071</td>
<td>1.55</td>
<td>45.1</td>
<td>None / None</td>
</tr>
</tbody>
</table>
From Table 4, the effect of adding filler to the liquid composition can be seen. The mechanical features were modified in such way that the tensile strength was increased, and the elongation at break was considerably reduced, compared to the liquid compositions where no filler was used. See Examples 8 and 9 versus Examples 1 and 7.

In spite of the decrease in the elongation at break in the samples with filler (Examples 8 and 9), it was possible to peel off the film easily without having it break during its removal.

The following examples show the usage of a random styrene-butadiene copolymer emulsion with carboxyl functional groups and a "hard" polyurethane, which is a dispersion of aliphatic, carboxyl functionalized polyurethane (polycarbonate based).

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.072</td>
<td>3.6</td>
<td>15.4</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w) + Wax (5 % w/w) + None</td>
</tr>
<tr>
<td>8</td>
<td>0.082</td>
<td>4.42</td>
<td>9.16</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w) + Wax (5 % w/w) + MS (1.7 % w/w)</td>
</tr>
<tr>
<td>9</td>
<td>0.077</td>
<td>3.81</td>
<td>10.5</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w) + Wax (5 % w/w) + Talc (10 % w/w)</td>
</tr>
</tbody>
</table>

Example 10

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

793 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 50 grams of a 48 % solids aqueous dispersion of random styrene-butadiene copolymer (SBR) with carboxyl functional groups having a molecular weight higher than 20,000 g/mol and a polystyrene content about 38 % (ARLATEX 1215-E from Industrias Negromex, Altamira, Tamaulipas, Mexico); 50 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (7.85 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9.04 grams), based on the solid content of polyurethane dispersion, wax and SBR dispersion, of ultraviolet stabilizer (TINUVIN
5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of Theological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); and 17 grams of filler, specifically polymeric microspheres (EXPANCEL 461 WET 20d36 with a particle size from 20 to 30 micrometers and density of 36 +/- 3 kg/m³).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate, measuring 10 cm wide, 30 cm long and 3 mm thick, using a conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was peeled off, by hand, with a certain difficulty compared with the previous examples. This protective film was observed to be slightly more flexible than the films obtained in the previous Examples 1 - 9.

Example 11

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

743 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 100 grams of a 48 % solids aqueous dispersion of a random styrene-butadiene copolymer (SBR) with carboxyl functional groups having a molecular weight higher than 20000 g/mol and a polystyrene content about 38 % (ARLATEX 1215-E); 50 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (7.36 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (9.26 grams), based on the solids content of polyurethane dispersion, wax and SBR dispersion, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); and 17 grams of filler, specifically polymeric microspheres (EXPANCEL 461 WET 20d36 with a particle size from 20 to 30 micrometers and density of 36 +/- 3 kg/m³).

All the components were mixed for 60 minutes using a high torque stirrer with 3 bladed type propeller. The resulting liquid composition was applied to a glass plate.
measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 arm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was peeled off with greater difficulty than the film from Example 10.

Example 12

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

- 793 grams of a 33 % aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 50 grams of a 35 % solids aliphatic polycarbonate based "hard" polyurethane dispersion (NEOREZ 985 from DSM Neoresins, Waalkwijk, Netherlands); 50 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (8.38 grams), based on the total solids content of both polyurethane dispersions, of cross-linking agent (CX-100); 3 % by weight (8.84 grams), based on solids content of both polyurethane dispersions and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); and 17 grams of filler, specifically polymeric microspheres (EXPANCEL 461 WET 20d36 with a particle size from 20 to 30 micrometers and density of 36 +/- 3 kg/m³).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks, Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was easily peeled off, compared with Examples 10 and 11. The protective film was observed to be slightly more flexible than the films containing the styrene-butadiene copolymer (Examples 10 and 11).
Example 13

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

743 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 100 grams of a 35 % solids aliphatic polycarbonate based "hard" polyurethane aqueous dispersion (NEOREZ 985); 50 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (8.4 grams), based on the solids content of both polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (8.87 grams), based the solids content of both polyurethane dispersions and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); and 17 grams of filler, specifically polymeric microspheres (EXPANCEL 461 WET 20d36 with a particle size from 20 to 30 micrometers and density of 36 +/- 3 kg/m³).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was relatively easy to peel off compared to Examples 10 and 11. The protective film was observed to be slightly less flexible than the films containing styrene-butadiene copolymer (Examples 10 and 11).

The liquid compositions from Examples 8, 10, 11, 12, and 13 were applied to automotive paint coated metallic plaques measuring: 10 cm wide, 30 cm long, and 2 mm thick. These were dried at room temperature (22-26 °C) until they could be touched without leaving any fingerprints on the surface of the film. This time was recorded. Later, they were heated in a 60 °C oven for 3 minutes, and then cooled and equilibrated for 48 hours at room temperature, 22-26 °C. Next the peel strength of the protective films was evaluated, at an angle of 180° on samples having a width of 2.54 cm and a length of 30 cm using a Universal Electromechanical Testing Machine (Model 5564 from Instron, Norwood, MA, USA) with the crosshead speed set at 30 cm/min, over a distance of 5 cm.
Therefore, it was possible to obtain 4 measurements from the same metallic plaque. The reported values are the average of four such measurements. In Table 5 the results from this evaluation, as well as the dry to the touch times can be seen.

Table 5. Peel strength and dry to the touch times for Examples 8, 10, 11, 12, and 13

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Dry to touch time, min</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.082</td>
<td>99</td>
<td>12</td>
<td>PE/PTFE (4 % w/w)+ PEG (5 % w/w)+ Wax (5 % w/w)/ MS (1.7 % w/w)</td>
</tr>
<tr>
<td>10</td>
<td>0.081</td>
<td>332.35</td>
<td>11</td>
<td>PE/PTFE (4 % w/w)+ PEG (5 % w/w)+ Wax (5 % w/w)/ MS (1.7 % w/w)</td>
</tr>
<tr>
<td>11</td>
<td>0.079</td>
<td>704.25</td>
<td>13</td>
<td>PE/PTFE (4 % w/w)+ PEG (5 % w/w)+ Wax (5 % w/w)/ MS (1.7 % w/w)</td>
</tr>
<tr>
<td>12</td>
<td>0.080</td>
<td>235</td>
<td>12</td>
<td>PE/PTFE (4 % w/w)+ PEG (5 % w/w)+ Wax (5 % w/w)/ MS (1.7 % w/w)</td>
</tr>
<tr>
<td>13</td>
<td>0.079</td>
<td>151.9</td>
<td>13</td>
<td>PE/PTFE (4 % w/w)+ PEG (5 % w/w)+ Wax (5 % w/w)/ MS (1.7 % w/w)</td>
</tr>
</tbody>
</table>

The presence of the carboxyl functionalized styrene-butadiene co-polymer (Examples 10 and 11), imparts an opaque appearance to the film, and provides resistance to scratching, but it significantly increases the peel strength required to remove the film. The presence of 5 % polycarbonate based "hard" polyurethane also increased the peel strength (Example 12).

However, when the content of the polycarbonate-based polyurethane was increased to 10 % (Example 13), the peel strength decreased relative to the 5 % formulation (Example 12), and the dry to the touch time remained practically the same.

In the following examples, the effect of combining release agents and filler is shown.

Example 14

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature, 22-26 °C, with the following composition:
710 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 50 grams of glycerin, 50 grams of polyethylene glycol (PLURACOL E-400); 40 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); 3 % by weight (7.03 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (7.49 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); and 100 grams of filler, specifically talc (YELLOWSTONE 325).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plate measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was relatively easy to peel off compared to those films obtained in Examples 10 and 11. The protective film was observed to have an acceptable level of flexibility, compared to the films containing only polyethylene glycol (Examples 6 - 13).

Example 15

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

750 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 100 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (7.43 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (7.89 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TINUVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); and 100 grams of filler, specifically talc (YELLOWSTONE 325).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied to a glass plates
measuring: 10 cm wide, 30 cm long and 3 mm thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was easily peeled off, and was observed to be more flexible than the film of Example 14.

Example 16

1 Kg. of the liquid composition was prepared in a 2 liter glass beaker, at room temperature (22-26 °C) with the following composition:

730 grams of a 33 % solids aqueous dispersion of polyester based aliphatic and carboxyl functionalized polyurethane (RU-41206); 50 grams of wax (474N30); 20 grams of a mixture of polyethylene/poly(tetrafluoroethylene) (AQUAPOLYFLUO 411); 100 grams of polyethylene glycol (PLURACOL E-400); 3 % by weight (7.23 grams), based on the solids content of polyurethane dispersion, of cross-linking agent (CX-100); 3 % by weight (7.69 grams), based on the solids content of polyurethane dispersion and wax, of ultraviolet stabilizer (TIISILEVIN 5050); 0.15 % by weight (1.5 grams), based on the total weight of the liquid composition, of rheological modifier (VISCALEX VH30); and 100 grams of filler, specifically talc (YELLOWSTONE 325).

All the components were mixed for 60 minutes using a high torque stirrer having a 3 bladed type propeller. The resulting liquid composition was applied on glass plate measuring: 10 cm wide, 30 cm long and 3 m thick; using a conventional spraying system (Spray gun from Binks Glendale Heights, IL, USA; Model 2001 with nozzle 66SD, PE needle and pressure of 2 atm). After drying for 24 hours at room temperature (22-26 °C), a protective film was obtained. This film was very easily peeled off compared with all the others examples. Regarding flexibility, the film generated in this example was almost the same as that of Example 15.

The liquid compositions from Examples 14, 15, and 16 were applied to automotive paint coated metallic plaques measuring 10 cm wide, 30 cm long, and 2 mm thick, and dried at room temperature (22-26 °C) until they could be touched without leaving any fingerprints on the surface of the film. This time was recorded. Later, they were heated in a 60 °C oven for 3 minutes, and then cooled and equilibrated for 48 hours at room temperature, 22-26 °C.
Next the peel strength of the protective films was evaluated, at an angle of 180° on samples having a width of 2.54 cm and a length of 30 cm, using a Universal Electromechanical Testing Machine (Model 5564 from Instron, Norwood, MA, USA) with the crosshead speed set at 30 cm/min, and a test length of 5 cm. Therefore, it was possible to obtain 4 measurements from the same metallic plaque. The reported values are the average of four such measurements.

In Table 6, the data regarding peel strength and dry to the touch times for the films obtained in Examples 14 - 16 are presented and the information from Examples 5, 6, and 7 is added for comparison.

Table 6. Peel strength and dry to the touch times from for Examples 5 - 7, and 14 - 16

<table>
<thead>
<tr>
<th>Example</th>
<th>Film thickness, mm</th>
<th>Peel Strength, g/in</th>
<th>Dry to touch time, min</th>
<th>Release Agent / Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.074</td>
<td>280</td>
<td>15</td>
<td>PE/PTFE (4 % w/w) + glycerin (5 % w/w)/ None</td>
</tr>
<tr>
<td>6</td>
<td>0.071</td>
<td>27.1</td>
<td>12</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)/ None</td>
</tr>
<tr>
<td>7</td>
<td>0.072</td>
<td>102.5</td>
<td>13</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)+ Wax (5 % w/w)/ None</td>
</tr>
<tr>
<td>14</td>
<td>0.076</td>
<td>161.6</td>
<td>17</td>
<td>PE/PTFE (4 % w/w) + PEG (5 % w/w)+ Wax (5 % w/w) + glycerin (5 % w/w)/ Talc (10 % w/w)</td>
</tr>
<tr>
<td>15</td>
<td>0.077</td>
<td>49.8</td>
<td>14</td>
<td>PEG (10 % w/w)+ Wax (5 % w/w)/ Talc (10 % w/w)</td>
</tr>
<tr>
<td>16</td>
<td>0.078</td>
<td>6.4</td>
<td>13</td>
<td>PE/PTFE (2 % w/w) + PEG (10 % w/w)+ Wax (5 % w/w)/ Talc (10 % w/w)</td>
</tr>
</tbody>
</table>

From Table 6 the effect of the use of glycerin (Example 14) can be seen to increase the protective film's peel strength and the dry to touch time. On the other hand, it can also be seen that the combination of polyethylene glycol with the mixture of polyethylene/poly(tetrafluoroethylene) (Example 16) results in a low peel strength for the resulting film and a relatively low dry to touch time.

The liquid composition from Example 16 was applied on a polycarbonate tail light and, after drying at room temperature (22-26 °C) during 24 hours, was peeled by hand.
The film was very easy to remove and it did not show any cracking, in spite of the curved shape of the tail light.

Spray paint (which contains toluene, acetone and xylene, all proven effective and common dissolution agents in acrylic paints) was applied over the protective film of Example 16 and the film was observed to be fairly resistant in terms of not suffering any degradation. In other words, it did not shrink, nor pierce, nor corrugate as a consequence of the applied aerosol paint.

The liquid compositions from Examples 7, 14, and 16 were applied by spraying to pieces of wood, coated with a polyurethane based varnish. These were dried and conditioned at room temperature (22-26 0C) for 48 hours. The resulting films were easily peeled off from the varnished wooden pieces.

Varnished wooden pieces, like those described above, were provided with protective films from the liquid compositions of Examples 7, 14, and 16 as described above. These protected wooden pieces were then placed in a Q-Fog saline chamber CCT 11 Model for one week at 35 0C, according to Standard ASTM B-1 17. At the end of this time, the samples were removed, and it was observed the films did not show any sign of degradation, such as fractures or cracking, thus protecting the wooden pieces.

Likewise, one half of a galvanized steel sheet was coated with the liquid composition from Example 16 and after drying for 48 hours at room temperature (22-26 0C) it was placed in a Q-Fog saline chamber CCT 11 Model for one week at 35 0C, according to Standard ASTM B-1 17.

The sample was then removed, and it was observed that the half of the sheet covered by the protective film did not show any sign of corrosion, whereas the half of the sheet that had not been protected exhibited corrosion on its surface.

From these results it has been shown that the peel strength of the protective films can be controlled by the formulation of the liquid composition.

Moreover, the protective film obtained from the liquid composition of the present disclosure, is capable of withstanding corroding environments, such as one of a salty fog.

The protective films obtained from the liquid compositions of the present disclosure have a broad range of use (service) temperature. In order to determine the service temperature, differential scanning calorimetry (DSC) was carried out using a Model Q100 DSC, from TA Instruments, New Castle, Delaware, with a ramp rate of
10 °C/min from -120 °C to 200 °C. Figure 1 shows the corresponding thermogram for the protective film, which was generated in Example 2.

As it can be seen from Figure 1, there is a glass transition [Tg] around -50 °C, corresponding to polyurethane, and a melting transition around 126 °C, corresponding to the polyethylene wax.

The window of use, in terms of temperature, is from -30 °C and up to 90 °C, without considerably affecting any mechanical capability of the film, particularly without suffering any softening, melting or cracking.

Furthermore, the flexibility as well as the mechanical and chemical resistance features of the protective films that were obtained by means of the crosslinking of the functional groups that were present in the polyurethane and/or the elastomer component, through the drying of the liquid composition, make it particularly appropriate for coating and protecting metallic, glass, ceramic or plastic articles. Such protective films exhibit the necessary flexibility that enables them to tolerate the distortion they are subject to during removal. Further, the chemical resistance of the protective films that are obtained from the liquid compositions of the present disclosure enables them to tolerate some chemical products, such as automotive paints, thereby making them suitable for use during the automobile repainting process, as a temporary masking material.

The protective film that is obtained from the liquid composition of the present disclosure is useful to temporarily protect metals like sinks, carbon steel pipes, stainless steel and aluminum, in general. It is useful when temporarily protecting metallic pieces of cars during their transportation from their place of manufacture to dealers.

Further, the protective film can be used to protect plastic pieces, such as polycarbonate, polymethylmethacrylate), and primarily stiff plastic pieces, against light scratching, some chemical products, dust and water.

Likewise, the film obtained from the liquid composition of the present disclosure can be used to temporarily protect glass and ceramic materials, against light scratching, some chemical products, dust and water.

Furthermore, the liquid composition matter of the present disclosure provides protective films with mechanical and chemical resistance features, particularly with a good resistance to corroding environments, such as those near sea coasts, which make it quite useful as a temporary protective coating for substrates such as wood, which may be coated
with paint or not, or with polyurethane or acrylic based coatings. For instance, the film that is obtained from the liquid composition of the present disclosure may be useful in protecting yachts during their transport.

The quoted examples are not restrictive, and variations thereof as might appear to be obvious to those skilled in the field of this disclosure are also included.
What is claimed is:

1. A liquid composition that provides a removable film for temporary protection, which comprises an aqueous dispersion of functionalized polyurethane resin, a release agent and a cross-linking agent.

2. The liquid composition, according to claim 1, characterized in that its polyurethane resin is aliphatic and it is derived from polyester or polyether or it has polycarbonate material in its structure.

3. The liquid composition, according to claim 1, characterized in that its polyurethane is an aqueous dispersion with a solids content of from 25 to 55 % by weight.

4. The liquid composition, according to claim 1, characterized in that the polyurethane dispersion content in the liquid composition varies in a range of from 50 to 100 % by weight, based on the total weight of the liquid composition.

5. The liquid composition, according to claim 1, characterized in that its polyurethane resin is functionalized with carboxyl groups along its polymeric chain.

6. A removable temporary coating obtained from a liquid composition according to claim 1, characterized in that it resists chemical substances such as isopropanol, turpentine oil, gasoline and greases.

7. A removable temporary coating obtained from a liquid composition according to claim 1, characterized in that it is resistant to water and salt water.

8. A removable temporary coating obtained from a liquid composition according to claim 1, characterized in that it does not show fractures or cracking when it is exposed to water or a corrosive environment.
9. The liquid composition according to claim 1, characterized in that it can be applied by spraying, atomization, brush, roller or immersion methods, and other traditional coating methods.

10. The liquid composition according to claim 1, characterized in that its release agents are selected from the group consisting of: pentaerythritol, glycerin, an emulsion of oxidized polyethylene wax, poly(tetrafluoroethylene) emulsions, mixtures of polyethylene and poly(tetrafluoroethylene), diglycerol, triglycerol, polyethylene glycol, ethers and esters of ethylene glycol, beaver oil, polydimethylsiloxanes, and ethoxylated polydimethylsiloxanes.

11. The liquid composition according to claim 1, characterized in that its release agent is present in an amount between 0.2 and 50 % by weight based on the total weight of the liquid composition.

12. The liquid composition according to claim 1, characterized in that its cross-linking agent is selected from the group consisting of: melamines, aziridines, epoxysilanes, carbodiimides, or polyurethanes, preferably the polyaziridine and/or the methyl glycidoxypropyl diethoxy silane.

13. The liquid composition according to claim 1, characterized in that its cross-linking agent is present in an amount between 1 and 10 % by weight based on the total content of solids of the polyurethane dispersion.

14. The liquid composition according to claim 1, characterized in that its additive is a stabilizer agent against ultraviolet light, and it is present in an amount from 0.1 to 7 % by weight based on the content of solids of polyurethane dispersions.

15. The liquid composition according to claim 1, characterized in that its content of thickening agent is between 0.01 % to 1 % by weight based on the total weight of the of the liquid composition.
16. The liquid composition according to claim 1, characterized in that its filler agent is selected from the group consisting of: talc and polymeric microspheres.

17. The use of the liquid composition according to claim 1, to provide a temporary protective film for polymeric materials against light scratching, some chemical products, dust, and water.

18. The liquid composition according to claim 1, characterized in that it is capable to providing a flexible film for the temporary protection of a substrate, wherein film exhibits easy removal from the substrate, and a service temperature of -30 °C to 90 °C.

19. The use of the liquid composition according to claim 1, to provide a temporary protective film for metallic pieces against light scratches, some chemical products, dust, and water.

20. The use of the liquid composition according to claim 1, to provide a temporary protective film for wooden items, wherein said wooden items may further comprise a coating of paint or varnish.

21. The use of the liquid composition according to claim 1, to provide a temporary protective film for metallic materials, for protection against corroding environments.

22. The use of the liquid composition according to claim 1, characterized in that it can be applied to either polymeric, metallic, ceramic or glass pieces or items, with either curved or non flat shapes, by the use of methods such as spraying, atomization, brush or roller.

23. A removable temporary coating obtained from a liquid composition according to claim 1, characterized in that it can be removed easily, and without leaving any material on a substrate having a flat or curved shape.
24. The liquid composition according to claim 1, characterized in that the proportions of its components can be modified in order to provide a film whose peel strength is in the range of from 6 to 800 grams per inch, with 2.54 width samples.
A. CLASSIFICATION OF SUBJECT MATTER

C09J 175/04(2006.01)i, C09J 7/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility Models and applications for Utility Models since 1975
Japanese Utility Models and applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS(KIPO internal), USPAT, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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☐ Further documents are listed in the continuation of Box C  ☒ See patent family annex

* Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 06 AUGUST 2007 (06 08 2007)

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