Abstract:

Anionic polyurethane aqueous dispersions are prepared by reacting a prepolymer A, obtained from aliphatic or cycloaliphatic diisocyanates, polytetramethylene glycol and one or more anionic or potentially anionic polyols, with a chain extender B which is a diamine sulfonate salt; the dispersion have a medium particle size above 600 nm and give films of high opacity and soft-feel touch which are useful for the coating of leather, fabrics, paper, cardboard, plastic, wood and metals.
ANIONIC POLYURETHANE AQUEOUS DISPERSIONS

The present invention relates to aqueous anionic polyurethane dispersions and to their use as filming agents for the coating of rigid or flexible objects in order to obtain opaque, soft-touch surfaces.

The aqueous dispersions of the invention can be used in the finishing of leather, for the superficial treatment of fabrics, paper, cardboard, plastic, wood and metals.

According to one of the fundamental aspects of the present invention the procedure of preparation of such aqueous polyurethane dispersions is described.

These dispersions are completely free from solvents and from the normally used opacifying additives, such as silica, silicates or polymeric particles.

STATE OF THE ART.

The surface of many manufactured articles, by way of example made from woven fabrics, leather, paper, plastic, wood and metal, is treated with the purpose of making it more homogenous, or of protecting it from the wear of the time or the atmosphere and/or in order to improve the certain aesthetic properties, such as high or low opacity, soft or rough touch, different colours, and so on.

Normally these effects are obtained through the application of dispersions of polymers containing several specific additives, as reported for example in "Tanning - dyeing - finishing" 4th edition, Bayer AG, p. 175-185 (1986).

In case of polyurethane dispersions, a greater opacity can be obtained, by way of example, by the addition of opacifying particles. These
opacifying particles can be silica particles, as described in patent US
6,284,836, or polymer particles, as described in US 6,649,487.
Nevertheless, the addition of heterogeneous particles has the
disadvantage of destabilizing the polymer compositions and of increasing
the brittleness of the film.
Moreover during the application a separation of the heterogeneous
materials can occur with consequent heterogeneity of the optical effect
along the surface of the treated material.
The use of amorphous or crystalline silica in order to increase the degree
of opacity in the final manufactured article is moreover dangerous for the
operators’ health, if the necessary safeguards measures are not carefully
applied.
The siliceous particles, because of their extreme fineness and volatility, are
in fact the object of continuous studies from national medical institutes of
research for the risk of pulmonary diseases that they can provoke.
In the literature many methods are reported that avoid the use of
opacifying particle; US 2006/01 11538, as an example, describes the use of
compositions based on a self-reticulating polyurethane that allow to
obtain products with a gloss below 40.
Another superficial characteristic which is more and more appreciated by
the market is the soft touch effect or velvet effect.
EPI, 489, 120, as an example, describes a photo-curable polyurethane
emulsion which is able to produce films with good stability and soft touch.
Also WO 2006/072080 describes a polyurethane formulation useful for
giving a soft and silky effect (“satinized and rubberish touch”) on rigid
surface. To this formulation, obtained from the reaction of a lucid polyurethane dispersion with a reticulating agent, an opacifying agent (Siθ2) is added in order to obtain a coating with a low degree of gloss (see Table 1).

It has now been surprisingly been found that it is possible to obtain an aqueous dispersion of an anionic polyurethane, free from organic solvents, that, without opacifying additives, is able to give durable films having high opacity and soft touch at the same time.

The coating obtained by means of the dispersion of the present invention is extremely innovative, since the high degree of opacity is obtained by means of the stable and homogenous (or easily re-dispersible) dispersion that does not develop persistent sediments over the time.

SUMMARY OF THE INVENTION

It is a fundamental object of the present invention an aqueous dispersion containing from 20 to 50% by weight of an anionic polyurethane prepared by reacting:

- a prepolymer A) containing from 5 to 25 meq/100 g dry weight of carboxylic groups obtained from:
  - one or more aliphatic or cycloaliphatic diisocyanates;
  - polytetramethylene glycol with molecular weight comprised between 500 and 3000 g/mol;
  - one or more anionic or potentially anionic polyols having two or more reactive groups toward the isocyanate group and at least one carboxylic or carboxylate group;
IV) optionally one or more nonionic polyols having two reactive hydroxy groups and a molecular weight comprised between 80 and 2000;

V) optionally one or more nonionic polyols having more than two hydroxy groups and a molecular weight comprised between 64 and 3000,
in such proportions that: a) the ratio between isocyanate groups NCO of 1) and the sum of reactive OH groups of II), III) and IV) is between 1.2 and 2.5; b) polytetramethylene glycol represents in moles at least 70%, preferably 90%, more preferably 100% of the molar sum of components II), IV and V); c) I), II), III), IV) and V) is equal to 100% of the components of the prepolymer with a chain extender b) chosen among diamine sulfonate salts having one or more sulfonic acid groups .

The aqueous dispersions of the present invention have a medium particle size above 600 nm, and preferably above 1000 nm, and give films of high opacity.

The expression "films of high opacity" means films with a gloss below 10 at a angle of 60 ° measured according to the standard method ISO 2813.

Another object of the present invention is a method for the preparation of aqueous dispersions containing from 20 to 50% by weight of an anionic polyurethane, with a medium particle size above 600 nm, preferably above 1000 nm, and able to produce films of high opacity, that comprises the following steps:
i) α prepolymer A) containing from 5 for 25 meq/100 g dry weight of carboxylic groups is prepared by reacting:
   i) one or more aliphatic or cycloaliphatic diisocyanates;
   ii) polytetramethylene glycol with molecular weight comprised between 500 and 3000 g/mol;
   iii) one or more anionic or potentially anionic polyols having two or more groups reactive toward the isocyanate group and at least one carboxylic or carboxylate group;
   IV) optionally one or more nonionic polyols having two reactive hydroxy groups and a molecular weight between comprised 80 and 2000;
   V) optionally one or more nonionic polyols having more than two hydroxy groups and a molecular weight comprised between 64 and 3000,
in such proportions that: a) the ratio between the isocyanate groups NCO of I) and the sum of reactive OH groups of II), III) and IV) is between 1.2 and 2.5; b) the polytetramethylene glycol represents in moles at least 70%, preferably 90%, more preferably 100% of the molar sum of components II), IV and V); c) the sum of I), II), III), IV) and V) is equal to 100% of the components of the prepolymer

ii) the prepolymer is dispersed in water by stirring;

iii) a chain extender B) chosen among diamine sulfonate salts having one or more sulfonic acid groups is added to the so obtained dispersion and it is allowed to react until all isocyanate groups disappear.
According to another aspect, the invention relates to the use of the aforesaid aqueous anionic polyurethane dispersions for the coating of leather, woven fabrics, paper, cardboard, plastic, wood or metals with film of high opacity.

Example 1 of US 6,077,897 describes a process for producing a waterborne polyurethane dispersion (WPU dispersion) by reacting 88 g of polytetramethylene glycol, 32 g of IPDI (which is a cycloaliphatic diisocyanate), 1.2 g of DMPA (a potentially anionic polyol having two or more groups reactive toward the isocyanate group and one carboxylic group), adding lithium diaminosulfonate and dropping water to the resulting system.

Although the process and dispersion of Example 1 of US 6,077,897 have features in common with the process and aqueous dispersions of the present invention, as a matter of fact, in Example 1 the content of anionic polyurethane in the dispersion is not reported, nor the molecular weight of polytetramethylene glycol or the ratio between the isocyanate groups NCO and the reactive OH groups in the prepolymer, nor the amount of lithium diaminosulfonate.

Therefore Example 1 of US 6,077,897 cannot be considered as an enabling disclosure of the process and aqueous dispersions of the present invention. Furthermore, the WPU dispersion of US 6,077,897 is used to prepare WPU/PEO (polyethylene oxide) composite electrolytes and not as soft-feel opaque coating.
Examples of diisocyanates useful for the present invention are 4,4'-dicyclohexyl-methane-diisocyanate, 1-isocyanate-3-isocyanate-methyl-3,5,5-trimethylcyclohexane (or isophoronediiisocyanate), hexamethylenediisocyanate, and mixtures thereof.

The preferred diisocyanates are 4,4'-dicyclohexyl-methane-diisocyanate, 1-isocyanate-3-isocyanate-methyl-3,5,5-trimethylcyclohexane (or isophoronediiisocyanate) and hexamethylenediisocyanate.

Polytetramethylene glycol with a molecular weight comprised between 500 and 1500 is preferred for the realization of the present invention.

Component IV) of the prepolymer A) is chosen among nonionic polyols having a molecular weight comprised between 80 and 2000 g/mol.

Preferably, the nonionic polyols are polyols polyethers or diols having a molecular weight below 150, like as an example propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol and mixtures thereof.

Component III) of the prepolymer A) is a carboxylic acid, preferably a carboxylic acid which is substituted in the position 2 by two hydroxymethyl groups; more preferably component III) is dimethylolpropanoic acid, dimethylolbutanoic acid or mixtures thereof.

Component V) of the prepolymer A) can be chosen among polyols having a molecular weight comprised between 64 and 1500 and functionality OH greater than 2; examples of utilizable substances are glycerin, pentaerythritol, trimethylolpropane and its derivatives, such as trifunctional polypropylene glycol, trifunctional polybutadienes and polyesters.
Trifunctional polyesters can be obtained from condensation reactions of diols with mixtures of difunctional and trifunctional acids, or of polyols with diacids.

In the prepolymer A) the ratio between the isocyanate groups NCO of I) and the sum of reactive OH groups of II), III) and IV) is between 1.2 and 2.5, preferably between 1.5 and 2.4.

The amount of carboxylic groups in the polyurethane is measured in milliequivalents (meq) of groups COOH and/or COO- for 100 g of prepolymer; in the anionic polyurethanes of the present invention this value is in the range 5 to 25, preferably in the range 10 to 25, and best results as degree of opacity are obtained when this value is comprised between 10 and 20.

In the method of the present invention the stage i) is preferably carried out in absence of organic solvents at a reaction temperature between 40 and 110°C.

The prepolymer obtained at the end of stage i) is normally neutralized, preferably with tertiary amines, like N-alkylmorpholine, tri-alkylamine, alkylalkanolamine, trialkanolamine and mixtures thereof, at a temperature below 90°C.

Triethylamine, dimethylethanolamine and N-methylmorpholine are particularly suited for this scope.

The neutralization can be carried out at the end of the reaction of synthesis of the prepolymer (step i)), in anhydrous environment, or during the subsequent dispersion in water of the prepolymer (stage ii)).
Step ii) is carried out adding the prepolymer to water (or to water and neutralizing agent) under mechanical stirring, optionally in the presence of an emulsifier.

The emulsifier can be chosen between nonionic, anionic and cationic surfactants.

Preferably the emulsifier is a nonionic surfactants.

Particular characteristic of the dispersion that is obtained at the end of step ii) is the high dimension of its particles; these in fact have a medium particle size above 600 nm, preferably above 800 nm and more preferably above 1000 nm.

The chain extender B) is a diamine sulfonate salt with one or more sulfonic acid groups neutralized and with at least 2 active hydrogens toward the NCO group, used in such amount that at least 3%, preferably from 3 to 50%, most preferably from 5 to 50%, of the free NCO groups contained in the prepolymer A) react with it; the sulfonate diamine salt can be used in mixture with a nonionic diamine with active hydrogens toward the NCO group, such as, as an example, with hydrate of hydrazine, ethylenediamine and mixtures thereof.

Particularly useful for the realization of the present invention are the diamine sulfonate of general formula X - NH - Ri - NH-R2-SO3- Y⁺, where Ri, R2 can be the same or different and are chosen between methylene, ethylene, propylene, phenylene; X is H or - R2SO3⁻.

The preferred neutralizers (Y⁺) of the diamine sulfonate are sodium, lithium or potassium cations.
Step iii), the extension of chain carried out with the diamine sulfonate increases the stability and above all the re-dispersibility (in case of sediment on the bottom) of the dispersion, without changing the particle size of the dispersion of the prepolymer: this guarantees at the same time that the dispersions so prepared produce a film with high opacity.

Examples of diamine sulfonate utilizable are salts of alkaline metals of 1,1-diaminomethanesulfonic acid, of 1,1-di(amo)neethyl)ethanesulfonic acid, of 2-[(2-aminoethyl) amino]ethanesulfonic acid, of 3-[(2-aminoethyl)amino]propanesulfonic acid, of diaminobenzenesulfonic acids, diaminomethanesulfonic acid, 1,1-diaminopropanesulfonic acid, 1,2-diaminopropanesulfonic acid.

Preferably the component B) is chosen among sodium salts of 2-[(2-aminoethyl)amino]ethanesulfonic acid, of 3-[(2-aminoethyl)amino]propanesulfonic acid, their adduct and mixtures thereof.

According to a preferred embodiment, the component B) is the sodium salt of 2-[(2-aminoethyl)amino]ethanesulfonic acid.

Step iii) of the method of the invention is carried out percolating the component B) in the dispersion of the prepolymer A), maintained under stirring, at temperature below 40 °C.

Following this procedure a milky dispersion of an anionic polyurethane with a medium particle size above 600 nm is obtained.

The particles have an elevated but controlled medium particle size that guarantees, like shown in the examples, the stability over the time or the re-dispersibility of the final dispersion.
After the extension the anionic polyurethane dispersion prepared with the procedure described above can be thickened with the addition of an opportune polymeric thickener, preferably chosen between the polyurethanes, or acrylic polymers, or derivatives of modified polysaccharides.

The expression polymeric thickener means a polymer that dosed at a concentration of 1% by weight is able to increase the Brookfield® viscosity of its aqueous solution of at least 200 mPa*s.

The most appropriate thickeners for this invention show a pseudoplastic rheologic behavior, they are preferably associative polyurethanes or acrylic polymers at a concentration comprised between 0.1 and 5% by weight of dispersion.

This thickening guarantees a more stable dispersion increasing at the same time the degree of opacity of the films obtainable from it.

The viscosity of the anionic polyurethane aqueous dispersion of the present invention is generally comprised between 50 and 2000 mPa*s.

Non-opacifying additives can be added to the so obtained anionic aqueous polyurethane dispersion in order to otherwise improve its performance, such as, as an example, its filming capacity, dimming, the development of "orange peels" effects or "fish-eyes" and foam reduction.

Some of these non-opacifying additives are supplied for example by ByK Chemie or Evonik, as it is known to those skilled in the art.

Examples of levelling and anti-slip additives that can be added to the aqueous dispersion are additives of the polisiloxane or silicone type.
The aqueous dispersions of the present inventions are stable or easily re-dispersible.

The aqueous dispersions are defined stable when they remain homogenous stored in a jar closed in an oven at 50°C for 14 days.

The aqueous dispersions are defined re-dispersible when, stored in a jar closed in an oven at 50°C for 4 days, they develop a sediment which is dispersible by the simple manual shaking of the jar.

The anionic polyurethane aqueous dispersions of the present invention can be reticulated with all reticulating agents known to those skilled in the art, such as with hydrodispersible polyisocyanates, polyaziridines, carbodiimides, epoxysilanes.

Reticulating agents are generally added in an amount comprised between 1 and 10% on dry weight of the dispersion.

The cross-linking does not modify the opacity of the films that are obtained from the dispersions, but can be useful in order to increase the mechanical and chemical properties of the films.

After spray application on black polish card, the film forming anionic polyurethane aqueous dispersions of the present invention have gloss below 10, measured at 60° as indicated in the standard method ISO 2813, and are advantageously utilisable in the finishing of leather, in the superficial coating of woven fabrics and paper and in the coating of plastics, such as polycarbonates and PVC, wood and metals.

The materials coated with films obtained from the aqueous dispersions of the invention can be used on car interiors to cover the instrumentations or
of the internal side of car doors, on electronic products like mobile phones, i-pod® and PDA.

The films obtained from the dispersions, by applying at least 3 g/m², preferably from 5 to 10 g/m² of anionic polyurethane, show high opacity and soft touch, without using solid opacifying additives.

In the examples that follow the preparation of aqueous dispersions according to the present invention (Example I-a and I-b) and aqueous dispersions prepared using components or amount of reagents different from those indicated in the present invention (Examples from II to V) is reported.

The particle size of the dispersions has been measured by means of Laser Correlation Spectroscopy (LCS) with a Coulter N4 Plus at temperature 25°C and angle 90°.

The dry matter has been determined with an IR dryer, Mettler Toledo HB 43, at a temperature of 160°C.

The quality of the process is determined also by filtrating the final dispersion with a 300 micron canvas; the behaviour during the filtration has been classified with a scale 1-3 (1 - without residues, fast; 2 - thin residues, 3 - film forming residues).

The stability has been determined by means of an aging test in oven for 14 days at 50°C and classified with a scale from 1 to 4 (1 - stable, 2 - sediment, 3 - sediment and partial water separation, 4 - total separation)

The re-dispersibility of the dispersion has also been estimated after the aging test in oven (yes = dispersed after manual shaking of the jar, no= not dispersed after manual shaking of the jar).
The gloss has been determined by means of application on a black card and measured at 60°, following the ISO standard method indicated above.

In an applicative example the comparison between the results of a finishing treatment on a leather substrate carried out using a commercial product combined with an opacifying silica or with the dispersion obtained in the I-a example like from invention is showed. The resistance to wet and dry rubbing, the resistance to folding, the point of black, the gloss and the soft-feel effect have been determined.

The resistances to wet and dry rubbing have been determined with a VESUCRUB FASTENSS TESTER VESLIC I.U.F. /450 following the standard method ISO 11640.

In the fold test the skin piece is folded repeatedly after drying in order to estimate stickiness and bleaching.

Opacity is determined as gloss at an angle of 60°.

The soft feel effect is determined by a panel test.

EXAMPLES

The following materials, as listed bellow, were used in the examples described afterwards.

Macrodiol 1 = poly(tetramethylene ether) glycol, molecular weight 1000 g/mol.

Macrodiol 2 = polypropylene glycol, molecular weight 1000.

Macrodiol 3 = poly(adipate-phthalate-1.6-hexane)diol, molecular weight 1000.

Acid = dimethylolpropanoic acid, molecular weight 134.20,
Diisocyanate = isophorone diisocyanate, molecular weight 222.30 (IPDI),

Diamine 1 = hydrazine hydrate, PM 32.01 (II),

Diamine 2 = 2-[(2-aminoethyl)amino]ethanesulfonic acid, PM 222 (EVS), sodium salt

Thickener 1 = polyacrylic, SIPACRIL 2723 OF, (Lamberti SpA, Italy)

Thickener 2 = polyurethane, VISCOLAM 1022, (Coatex, France)

Silica = LAMFILLER 4067, amorphous silica compound, water dispersed (Lamberti SpA, Italy)

Amine = triethylamine, PM 101.15 (TEA)

Surfactant = ethoxylated linear alcohol Cio-Ci ô 8 moles of ethoxy groups.

EXAMPLE I-a, I-b

Preparation of an anionic dispersion according to the described procedure.

Table 1 - Formulations (examples according to the invention)

<table>
<thead>
<tr>
<th></th>
<th>Example I-a</th>
<th>Example I-b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mmol</td>
</tr>
<tr>
<td>MACRODIOL 1</td>
<td>181.8</td>
<td>220</td>
</tr>
<tr>
<td>MACRODIOL 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ACID</td>
<td>6.9</td>
<td>62</td>
</tr>
<tr>
<td>DIISOCYANATE</td>
<td>98.5</td>
<td>536</td>
</tr>
<tr>
<td>WATER</td>
<td>543.0</td>
<td>-</td>
</tr>
<tr>
<td>DIAMINE 1</td>
<td>31.5</td>
<td>191</td>
</tr>
<tr>
<td>DIAMINE 2</td>
<td>27.7</td>
<td>51</td>
</tr>
<tr>
<td>THICKENER 1</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>THICKENER 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solid content, %</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Rm [NCO/OH]</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>meq/100 g of solid</td>
<td>16.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>
18.1.8 g (220 mmol) of Macrodol, 6.9 g (62 mmol) of Acid and 0.1 g of phosphoric acid (concentration 85%) are loaded in a reactor equipped with thermometer, stirrer and condenser, under nitrogen atmosphere and at room temperature.

98.5 g (536 mmol) of Diisocyanate are added under stirring after approximately 10 minutes of homogenization of the mixture at 40°C.

The reaction mixture is then heated up and maintained for 60 minutes at 60°C.

The reaction is carried out at 80°C, until the content of NCO groups in the prepolymer is 6.1 2%.

The titration of the residual isocyanate groups has been determined in this and all the other examples according to the norm ASTM D2572.

Once reached the required value of NCO groups the prepolymer is cooled down.

At approximately 75°C 5.3 g of neutralizing agent Triethylamine (62 mmol) are added under stirring.

After about 10 minutes, the prepolymer is dispersed in 543 g of demineralized water under strong stirring and temperature below 35°C.

The extension is carried out adding Diamine 1 and Diamine 2 as described in Table 1 at temperature below 35°C.

The obtained polyurethane dispersion is then filtered with a 300 µm canvas and brought to a dry content of 32% (Example l-b). In the Example l-a, before being filtered, the dispersion is thickened with 20.0 g of Thickener 1 diluted in water 1/4.
EXAMPLES II - V

The procedure described in the Example I-a is followed, but modifying the ratios and the raw materials as shown in Table 2.

The obtained dispersions are thickened with 15.0 g of Thickener 1.25% in water, and 5.0 g of Thickener 2.

The diameter of the particles, the solids content, the quality of the filtration, the stability and the re-dispersibility of the obtained dispersions and the gloss at 60° of films on a glossy-black carton are reported in Table 3.

Table 2 - (comparative Examples H-V)

<table>
<thead>
<tr>
<th></th>
<th>Example II</th>
<th>Example III</th>
<th>Example IV</th>
<th>Example V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mmol</td>
<td>g</td>
<td>mmol</td>
</tr>
<tr>
<td>MACRODIOL 1</td>
<td>212.5</td>
<td>220</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MACRODIOL 2</td>
<td>-</td>
<td>-</td>
<td>212.3</td>
<td>220</td>
</tr>
<tr>
<td>MACRODIOL 3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ACID</td>
<td>7.8</td>
<td>55</td>
<td>7.8</td>
<td>60</td>
</tr>
<tr>
<td>DIISOCYANATE</td>
<td>112.0</td>
<td>522</td>
<td>114.1</td>
<td>532</td>
</tr>
<tr>
<td>WATER</td>
<td>602.4</td>
<td>-</td>
<td>612</td>
<td>-</td>
</tr>
<tr>
<td>DIAMINE 1</td>
<td>49.8</td>
<td>247</td>
<td>38.0</td>
<td>189</td>
</tr>
<tr>
<td>DIAMINE 2</td>
<td>-</td>
<td>-</td>
<td>32.1</td>
<td>50</td>
</tr>
<tr>
<td>THICKENER 1</td>
<td>15.0</td>
<td>-</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>THICKENER 2</td>
<td>5.0</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Solid content, %</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Rm (NCO/OH)</td>
<td>1.9</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>meq/100 g of solid</td>
<td>15.1</td>
<td>16.5</td>
<td>32.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>

The prepolymers of examples IV and V were prepared with 4% of solvent (N-methylpyrrolidone).
Table 3 - Characteristics of the dispersions

<table>
<thead>
<tr>
<th>Example</th>
<th>I-a</th>
<th>I-b</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARTICLES DIAMETER, nm</td>
<td>1300</td>
<td>1200</td>
<td>850</td>
<td>85</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>SOLID CONTENT, %</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>FILTRATION *</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>STABILITY **</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>RE-DISPERSIBILITY***</td>
<td>-</td>
<td>yes</td>
<td>not</td>
<td>yes</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GLOSS 60°</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6</td>
<td>25.5</td>
<td>79.6</td>
<td>18.7</td>
</tr>
</tbody>
</table>

* 1 - without residue, fast, 2 - fine residue, 3 - film-forming residue
** 1 - stable, 2 - sediment, 3 - sediment and partial water separation, 4 - coagulation, total separation
*** yes - after manual shaking of the jar, not - does not re-disperse after manual shaking of the jar

APPLICATION EXAMPLE

The mechanical properties of two leathers treated with polyurethane dispersions were compared. The dispersions used were: i) glossy polyurethane dispersion - commercial product of Lamberti SpA (Rolflex DL48) mixed with 3 wt.% of silica with respect to the dry content of the dispersion (Leather 2) and ii) the same Rolflex DL48 with addition of the dispersion obtained in Example l-a (Leather 1). The amount of the dispersion obtained in Example l-a used for the Leather 1 is in order to obtain two leathers with the same degree of opacity.

The leather treated with the opacifying dispersion l-a shows better properties in comparison to the standard opacifying agent based on silica, in particular for rubbing fastness, both dry and wet, and the resistance to folding (see Table 4).
Table 4 - Comparison between the properties of leather treated with the resin containing opacifying agent according to the invention and the standard one based on silica.

<table>
<thead>
<tr>
<th>Example</th>
<th>Leather 1</th>
<th>Leather 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubbing fastness (dry) after 50 rubbings</td>
<td>not polished</td>
<td>polished</td>
</tr>
<tr>
<td>Rubbing fastness (wet)</td>
<td>160</td>
<td>100</td>
</tr>
<tr>
<td>Resistance to folding</td>
<td>+1</td>
<td>0</td>
</tr>
<tr>
<td>Touch</td>
<td>soft</td>
<td>soft</td>
</tr>
</tbody>
</table>

0...similar to the comparative sample
+1...better than the comparative sample
CLAIMS

1) Aqueous dispersion having medium particle size above 600 nm containing from 20 to 50% by weight of an anionic polyurethane prepared by reacting:

a n anionic prepolymer A) containing from 5 to 25 meq/100 g dry matter of carboxylic groups prepared from:

ii) one or more aliphatic or cycloaliphatic diisocyanates;

ii) polytetramethylene glycol with molecular weight comprised between 500 and 3000 g/mol;

iii) one or more anionic or potentially anionic polyols having two or more reactive groups toward the isocyanate group and at least one carboxylic or carboxylate group;

IV) optionally one or more nonionic polyols having reactive two hydroxy groups and molecular weight comprised between 80 and 2000;

V) optionally one or more nonionic polyols having more than two hydroxy groups and molecular weight comprised between 64 and 3000,

in such proportions that: a) the ratio between isocyanate groups NCO of 1) and the sum of reactive OH groups of II), III) and IV) is between 1.2 and 2.5; b) polytetramethylene glycol represents in moles at least 70% of the molar sum of components II), IV and V); c) the sum of I), II), III), IV) and V) is equal to 100% of the prepolymer components

with
α chain extender B) chosen among diamine sulfonate salts having or more sulfonic acid groups.

2) Aqueous dispersion of claim 1) in which the anionic polyurethane is prepared by reacting an anionic prepolymer A) containing from 10 to 25 meq/1 00 g dry matter of carboxylic groups.

3) Aqueous dispersion of claim 2) in which the prepolymer A) contains from 10 to 20 meq/1 00 g dry matter of carboxylic groups.

4) Aqueous dispersion of any of claims from 1) to 3) in which the chain extender B) is in such an amount that at least 3% of free NCO groups in the prepolymer A) react with it.

5) Aqueous dispersion of claim 4) in which the nonionic polyols IV) are diols with a molecular weight below 150 or polyether polyols.

6) Aqueous dispersion of claims 4) or 5) in which polytetramethylene glycol represents in moles at least 90% of the molar sum of components II), IV) and V) of the prepolymer A).

7) Aqueous dispersion of claims 4) in which the polytetramethylene glycol represents in moles 100% of the molar sum of components II), IV) and V) of the prepolymer A).

8) Aqueous dispersion of claim 6) or 7) having a medium particle size above 1000 nm.

9) Aqueous dispersion of any of the previous claims containing from 0.1 to 5% by weight of a thickening polymer.

10) Method for the preparation of aqueous dispersions containing from 20 to 50% by weight of an anionic polyurethane having medium particle size
above 600 \( \pi \) m and able to produce films of high opacity that comprises
the following steps:

i) a prepolymer A) is prepared containing from 5 to 25 meq/1 00 g of
carboxylic groups reacting:

i) one or more aliphatic or cycloaliphatic diisocyanates;

ii) polytetramethylene glycol with molecular weight comprised
between 500 and 3000 g/mol;

iii) one or more anionic or potentially anionic polyols having two or
more groups reactive toward the isocyanate group and at least
one carboxylic or carboxylate group;

iv) optionally one or more nonionic polyols having two reactive
hydroxy groups and a molecular weight between comprised 80
and 2000;

v) optionally one or more nonionic polyols having more than two
hydroxy groups and a molecular weight comprised between 64
and 3000,
in such proportions that: a) the ratio between the isocyanate
groups NCO of i) and the sum of reactive OH groups of ii), iii) and
iv) is between 1.2 and 2.5; b) the polytetramethylene glycol
represents in moles at least 70%, preferably 90%, more preferably
the 100% of the molar sum of components ii), iv and v); c) the sum
of i), ii), iii), iv) and v) is equal to 100% of the components of the
prepolymer

ii) the prepolymer is dispersed in water under stirring;
iii) α chain extender B) chosen among diamine sulfonate salts having one or more sulfonic acid groups is added to the dispersion so obtained in such an amount that at least 3% of free NCO groups in the prepolymer A) react with it and it is allowed to react until all the isocyanate groups disappear.

11) Method for the preparation of aqueous dispersions of claim 10) in which the prepolymer A) prepared in step i) contains from 10 to 25 meq/100 g of carboxylic groups.

12) Method for the preparation of aqueous dispersions of claim 11) in which the prepolymer. A) prepared in step i) contains from 10 to 20 meq/100 g of carboxylic groups.

13) Method for the preparation of aqueous dispersions of any of claims from 10) to 12) in which in step iii) the chain extender B) is added in such an amount that between 3 and 50% of free NCO groups contained in the prepolymer A) react with it.

14) Method for the preparation of aqueous dispersions of claim 13) in which in step iii) the chain extender B) is added in such an amount that between 5 and 50% of free NCO groups contained in the prepolymer A) react with it.

15) Use of aqueous dispersions as described in claims from 1) to 9) for the coating of leather, fabrics, paper, cardboard, plastic, wood or metals with films of high opacity.