

WATER DISPERSIBLE POLYURETHANE PELLETS: THE NEW PU DISPERSION PRODUCTION TECHNOLOGY

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INTRODUCTION

MERQUINSA, a Spanish company located in Barcelona has been dedicated since its foundation, 38 years ago, to the research, production and sale of polymers. Polyurethanes have always been paid a special attention by MERQUINSA and have become the only polymers the company has been dedicated to for the last ten years, because their special characteristics have allowed a growth in their consumption since they were marketed in the fifties, that has been continuous and sometimes spectacular.

Thanks to the great versatility of the family of polyurethanes, allowed by the possibility of using a wide range of raw materials, high quality polymers are obtained, that can be used in a wide variety of sectors: from shoe, wood or automotive adhesives to extruded pneumatic tubes or high quality injected parts, as well as textile coatings and paints, or as a component in various formulations for hot-melts, inks, etc.

In the adhesives market, on which we will focus our paper, MERQUINSA has always been present and offering highly specialised products to its customers, as a result of a continued research embracing the chemical structure of polyurethanes and their applications as well, allowing MERQUINSA to offer an excellent technical service to its customers. The purpose of this paper is to describe the two main types of polyurethane crystalline adhesives (solvent based and water based), depicting the different structures and conventional production methods for both systems. Thereafter a new technology will be presented, that has been developed in Merquinsa and is patent pending, for the production of polyurethane aqueous dispersions, with their resulting advantages over the conventional dispersions that are marketed at present.

POLYURETHANE IN SOLVENT MEDIUM OR POLYURETHANE IN AQUEOUS MEDIUM?

Polyurethane adhesives can be found basically in 2 forms:
Polyurethane solution in organic solvents
Polyurethane dispersion in aqueous, solvent-free medium.

Since polyurethane aqueous dispersions have appeared in the early eighties, the advantages and drawbacks of both systems have given rise to abundant literature and discussions. The enclosed table (Table 1) summarizes their main characteristics.

The solvent based adhesives are more stable than the water-based adhesives, although they show safety, toxicity and environmental contamination problems which induces progressive governmental regulations to tend to limit the use of solvents. The use of "green" solvents, not aggressive to the environment becomes every day more necessary, if we have to adapt to such regulations.

Regarding the chemical nature of polyurethanes, the water based polyurethanes are applied with a higher solids content, compared to the solvent based polyurethanes, because their viscosity does not depend on the molecular weight of the polyurethane, as is the case for solvent based polyurethanes.

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	Solvent based	Water based
% Solids	15-18 %	40-50 %
Isocyanate	Aromatic	Aliphatic
Polar ionomeric groups	No	Yes
Toxicity	Yes	No
Environmental contamination	Yes	No
Drying time	Short (not much energy required)	Slow (more energy required)
Flammability or explosion hazards	Yes	No
Stability at low temperatures	Yes (Reversible freezing)	No (Irreversible freezing)
Stability of adhesive	High	Medium
Crosslinking agent needed	No	Yes
Adhesive properties	Excellent	Excellent

Table 1- Characteristics of solvent based adhesives versus water based adhesives

However, the kind of isocyanate that is used generally is different in both types of polyurethanes: the solvent based polyurethanes are mostly aromatic (mainly MDI-based) whereas the water based polyurethane dispersions, due to the characteristics inherent to their production process that will be detailed later on, are made of aliphatic polyurethanes (mainly IPDI or HDI based). Another important difference in their structure is the presence of polar ionomeric groups (mainly carboxilate or sulphonate) in the polymeric chain of the water based polyurethane. Such ionomeric groups are absolutely necessary for the formation of dispersions, because they act as internal surfactants, and cannot be found in the chain of the solvent-based polyurethanes. The differences in the structure that are due to such ionomeric groups will be further commented later on.

HOW ARE A SOLVENT BASED AND A WATER DISPERSION PRODUCED?

The presentation and appearance of a solvent based polyurethane and an aqueous dispersion are, of course, very different.

The polyurethanes for the production of solvent-based adhesives are commercialized in form of 100 % solids pellets, the adhesive maker dissolves such pellets and obtains his own formulation. Aqueous dispersions are sold as such, with 40-50% solids and the adhesive maker uses them, in turn, for obtaining his own formulation. This involves the transport of the water contained in the dispersions (with a clear economic disadvantage), as well as a loss of stability of the polyurethane due to hydrolysis if the temperature conditions are not well controlled during transportation.

Logically, the production of both types of polyurethanes differs considerably, although the three basic components of any polyurethane are maintained in both:

- Diisocyanate (NCO-R-NCO)
- Long-chain diol with high molecular weight (OH-----R'-----OH)
- Short-chain diol (OH-R''-OH)

a) production of polyurethanes for solvent-based adhesives

The latest technology for the production of solvent-based polyurethanes consists in the continuous reaction of the three components in a reactor of extruder type that, with a special configuration of the screws, allows the reaction at the desired temperature.

The molecular weight of the polyurethane, the kind of long-chain diol, its molecular weight and the ratio of long-chain diol moles/short-chain diol moles will regulate the properties of the adhesive, as well as its solubility. Besides, the relationship between the diisocyanate moles and the sum of moles of both diols (NCO/OH relationship) will regulate the molecular weight of the polyurethane, since it is a polycondensation reaction. As a result, thanks to the very precise metering systems that allow to keep the NCO/OH ratio constant during the whole process, the desired molecular weight can be obtained and, thereby, the previously fixed viscosity of the polyurethane solution.

b) production of aqueous polyurethane dispersions

The different methods for the production of anionic polyurethane dispersions are well known. The most widely used are:

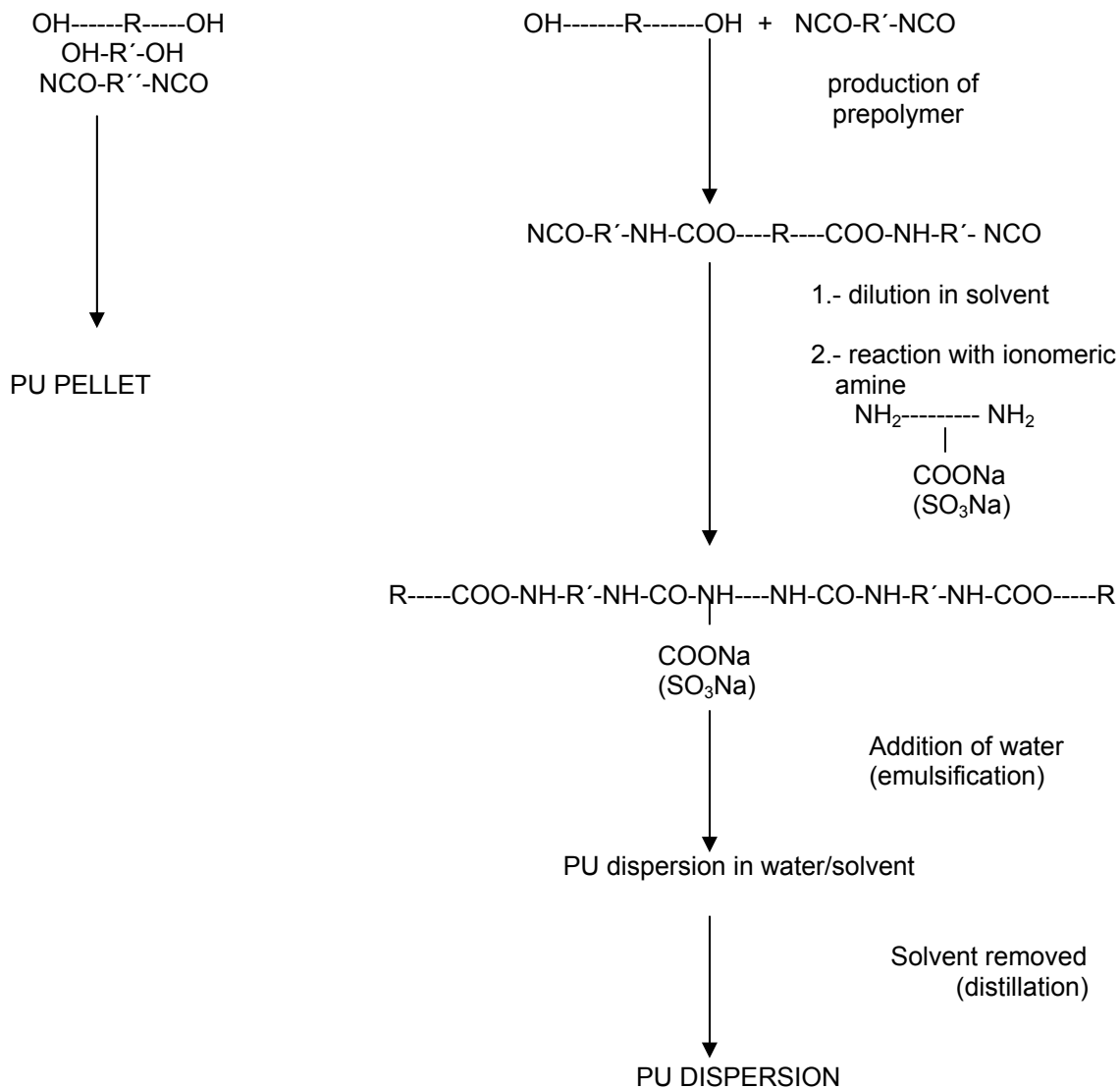
- acetone process,
- prepolymer emulsification process,
- melt dispersion process,
- cetimine-cetazine process

The most widely used are the two processes that are mentioned first. This paper will describe only the acetone process which is the one that is generally used for the production of crystalline polyurethane dispersions for adhesives, because it is the only system allowing a homogenous polyurethane formation, and thus a precise control of the molecular weight, which is a compulsory condition, if the desired adhesive properties are to be obtained.

This system consists in the previous production of a prepolymer (low molecular weight polyurethane with reactive NCO groups in the chain ends). Once the production of the prepolymer is achieved, it is solved in acetone and later on it is extended with ionomeric and non-ionomeric diamines until reaching the desired molecular weight, which can be controlled by the viscosity of the product. At the end, a monoamine is added, so as to avoid further extension of the polyurethane.

Water is then added to this dissolution of ionomeric polyurethane until its emulsification, and afterwards acetone is wholly distilled under vacuum. The particle size of the dispersion depends on the quantity of ionomeric groups that are found in the formulation.

A very general scheme of both processes would be as follows:



Generally speaking, the consistency of the polymer from batch to batch is higher for the production of polyurethane pellets than for the production of dispersions.

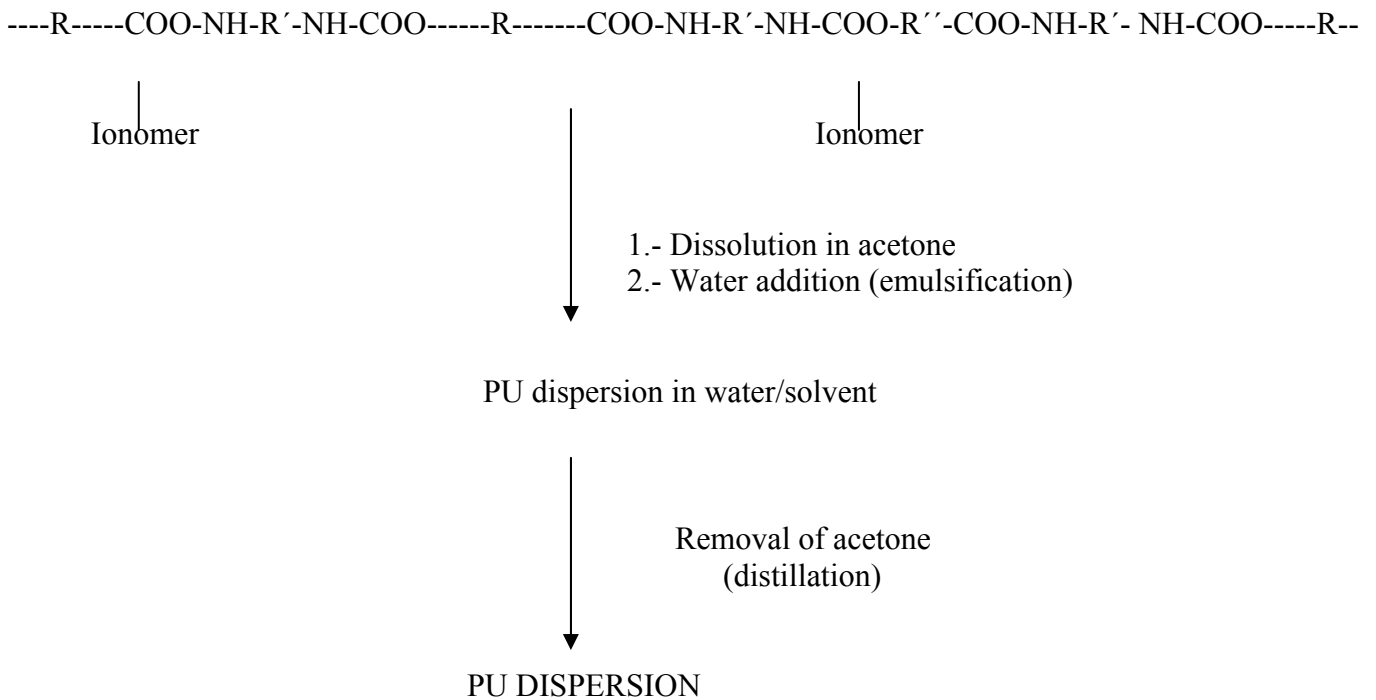
The production of a urethane prepolymer, necessary for the production of a dispersion, is a very delicate process which requires a very strict control of the reaction kinetics, so as to avoid undesired secondary reactions, as well as the presence of unreacted free diisocyanate, which would result in quality problems of the dispersion. Diisocyanates with very reactive NCO groups and with very similar reactivity such as MDI do not allow a control of their reaction kinetics. This fact, in addition to the need of diluting ionomeric amines in water, and this latter reacts with very reactive NCO groups, makes it impossible to use aromatic diisocyanates and as a result, the production of aromatic dispersions by this process is not feasible.

NEW TECHNOLOGY FOR THE PRODUCTION OF AQUEOUS POLYURETHANE DISPERSIONS

MERQUINSA, on the basis of its wide experience in the production of polyurethanes for solvent based adhesives as well as in the production of aqueous polyurethane dispersions, has developed a new system for the production of polyurethane dispersions that, embracing both processes, improves the classic acetone process and at the same time, opens to the adhesive maker a wide range of possibilities that were unknown so far.

This new technology consists basically in the production in accordance with the process described in the paragraph above, of 100% solid polyurethane pellets to which a ionomeric group has been added in its chains, so that these pellets can be dissolved in acetone. The resulting dissolution can be submitted to the classic emulsification process, allowing to eventually obtain a polyurethane dispersion.

The production scheme of such dispersion would be as follows:



This process, that we have called pellet-acetone process, in contrast with the classic prepolymer-acetone process, offers a series of advantages, that we will mention here below:

1. Possibility of production of aromatic polyurethane dispersions

Since the previous production of a prepolymer is not needed in this system, and neither is the presence of water at any stage of polymerization of the polyurethane, it is possible to produce (besides aliphatic dispersions) highly crystalline polyurethane aromatic dispersions, not available so far on the market.

This allows the use of aliphatic dispersions only when required by the given application.

2. The adhesive maker can produce the emulsion

As already seen, this new process consists of 2 phases that are clearly differentiated and that can take place at different times, because the polyurethane in the pellet is totally reacted.

This allows that whereas the production of the ionomeric pellet is a process carried out exclusively by MERQUINSA, the dissolution and later emulsification of the pellet is a process that can be carried out either by MERQUINSA or by some of the interested customers.

Thus, the sale of the ionomeric pellet by MERQUINSA, together with the easy emulsification process allow the user to produce his own dispersion, with the following advantages:

- Reduction of transport costs

The transport of a dispersion containing 50-60% water is replaced by the transport of 100 % solids pellets

- More stability of the adhesive

It is well known that the polyurethane dispersions, due to the fact that the polyurethane is in constant contact with water, have a lower hydrolysis stability than the pellets, which causes a slow reduction of the molecular weight of the polyurethane in emulsion, accompanied by an alteration in its adhesive properties, that does not happen with the polyurethane pellets. The same adhesive maker can produce the dispersion when he thinks it convenient, obtaining thus consistent adhesion values, since the hydrolysis process of the dispersion during transportation and storage is eliminated.

- The user can choose the dispersion he wants to produce

With the ionomeric pellet, under MERQUINSA's proper assessment, the user can select some external characteristics of the emulsion, This way, he can obtain different particle sizes (and thus different viscosities) or, varying the quantity of water used in the emulsification process, he can also obtain dispersions with different solids contents.

3. The acetone used in the process can be reused without being reprocessed.

As the polyurethane in the pellets is fully reacted, i.e. without reactive NCO groups, the requested grade of purity of the acetone in the dissolution is not so high as far as water content is concerned, as would be the case in the classic system.

If the distillation process is adequately regulated, most of the acetone that is distilled can be reused in the following process, without requiring a new distillation, which makes it easier to the very same user to produce the dispersion.

ADHESIVE PROPERTIES OF THE POLYURETHANE DISPERSIONS OBTAINED WITH THE NEW PRODUCTION TECHNOLOGY

In a first stage, MERQUINSA will market the following products resulting from the new technology just described, under the DISPERBOND brand:

DISPERBOND® D31S

Ionomeric aromatic polyurethane pellet, based on a polycaprolactone-polyester copolymer, out of which aqueous dispersions can be produced

DISPERBOND® D31W40 DISPERBOND® D31W50

Aromatic aqueous polyurethane dispersions with 40 and 50 % solids, based on a highly crystalline polycaprolactone-polyester copolymer, made out of DISPERBOND D31S.

In a second stage, our company is developing now a product of aliphatic nature .

MERQUINSA has also developed a crosslinking agent for this new line of emulsions:

QUIDUR® 444-20

Aliphatic , low viscosity, water emulsifiable polyisocyanate. Recommended (2-5% in weight on dispersion) crosslinking agent for increasing the heat resistance of the dispersions.

Next, the main properties of the DISPERBOND® D31W40 and DISPERBOND® D31W50 dispersions are detailed.

1. Crystallisation speed

The crystallisation speed measures the speed at which the polyurethane when cooled, is transformed from the melt or non-crystallised state to the crystalline state. The crystallised polyurethane has a much higher cohesion than the melt polyurethane, and that is why the crystallisation speed will indicate the speed at which the adhesive develops its maximum cohesion.

The crystallisation speed has been measured by the variation of the elastic shearing module of the polymer, when this is cooled at ambient temperature after staying at 80°C during 5 minutes. For such measurement, a thermal analyser with dynamic mechanical properties has been used, working at a frequency of 1 Hz.

For comparison purposes, the chart shows also the values obtained with a conventional polyurethane dispersion and a solvent based PU.

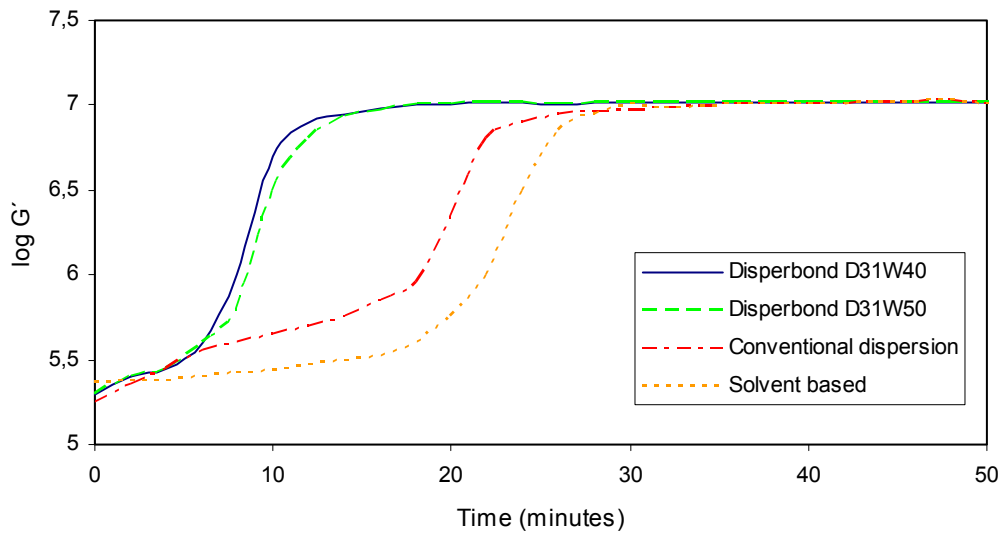


Fig. 1.- Crystallisation speed of Disperbond® D31W40, Disperbond® D31W50, conventional dispersion and a solvent based PU.

The high crystallinity grade of DISPERSION® can be observed in the chart.

2. Adhesives properties

The measurement of the adhesive properties has been done by thickening first the emulsion until reaching a viscosity of 1500-3000 mPas at 20°C, which is similar to the one of the adhesives of this kind which use to be found on the market. At the time of application, 3% of crosslinking agent QUIDUR® 444-20 have been added.

The application was carried out on plasticized PVC strips of 30x145 mm. with a dosing rod adequate for applying a quantity of adhesive of 33 gr./m2 of dry polymer. Such strips were dried at 23°C during 60 minutes. Once dry, they were activated at different temperatures with a flash lamp and then pressed during 15 seconds with a 1.6 bars pressure.

2a.- adhesion

The strips were unbonded 1 second (initial adhesion) and 72 hours (final adhesion) after being activated and pressed with an Instron 4464 dynamometer at a speed of 220 mm/min, with the results shown in the chart below:

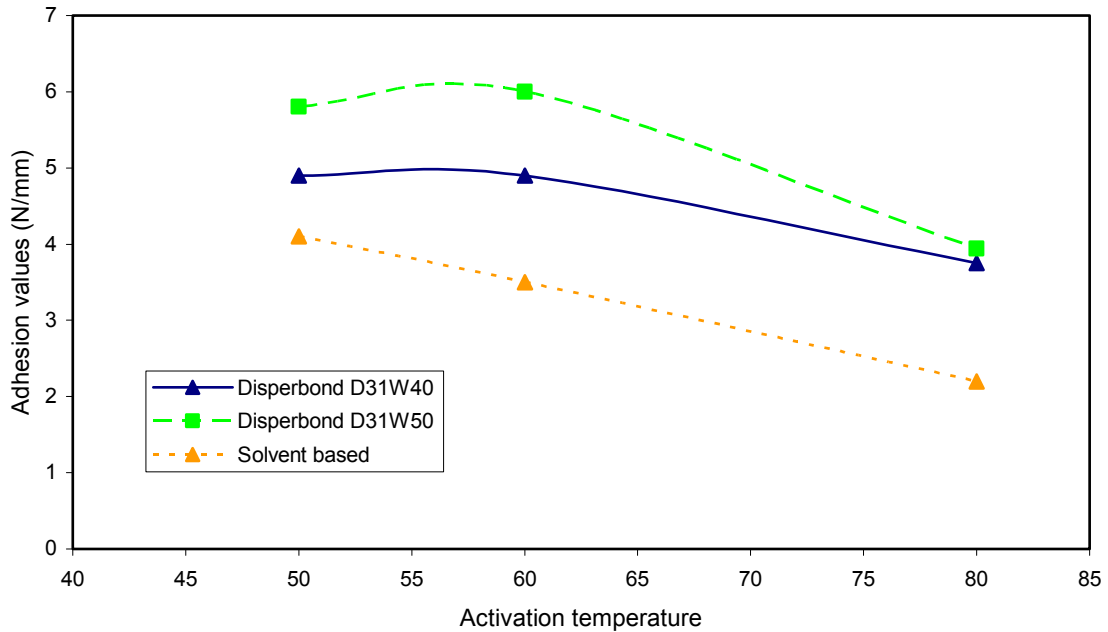


Fig. 2.- Adhesive values of Disperbond[®] D31W40 and Disperbond D31W50 related to the activation temperature, compared with a conventional solvent based PU.

DISPERBOND[®] shows excellent activation capabilities, with a maximum value between 50-60° and an initial adhesion level of 5-6 N/mm; values that are even higher than those obtained with solvent-based adhesives, due to the presence of ionic groups.

A right distribution of the ionic groups in an adequate polymeric chain, due to the important polarity differences between such highly polar ionic groups and the polymeric chain, give birth to a polyurethane with a high level of phase separation. As a result, the ionic groups form aggregates in microdomains with real physical crosslinks between themselves, which creates a considerable increase of the cohesion of the polyurethane hard segments, in comparison with the conventional, non ionic, hard segments (2). This fact, together with the increase of interactions between the polymer and the substrate due to the polar groups, as well as their high crystallinity, explain the high adhesion values of such dispersions.

2b.- resistance to heat

For this test, once the strips were pressed, they were kept during 72 hours at 23°C/50% r.h. They were thereafter introduced in an oven at 50°C (or 60°) during 1 hour, and then taken out of the oven, measuring at the same time the unbonding values of the strips.

The obtained values are as follows.

Temperature	Disperbond® D31W40	Disperbond® D31W50
50° C	2.47 N/mm	2.52 N/mm
60° C	1.76 N/mm	2.21 N/mm

Such values show that the adhesive has an excellent resistance to heat, which can be compared to the performances of the solvent based adhesives.

3. Stability

3a.- Stability of the adhesive values

The dispersion has been kept at a temperature of 23°C for 6 months and its adhesive values have been measured, so as to study its stability. The previously mentioned methods have been used. The following chart shows the initial adhesion values (activation temperature of 60°) and the heat resistance (oven temperature of 60°C).

Such values confirm a perfect stability of the dispersion at 23°C for a period of at least 6 months, keeping the most critical values unchanged during such period.

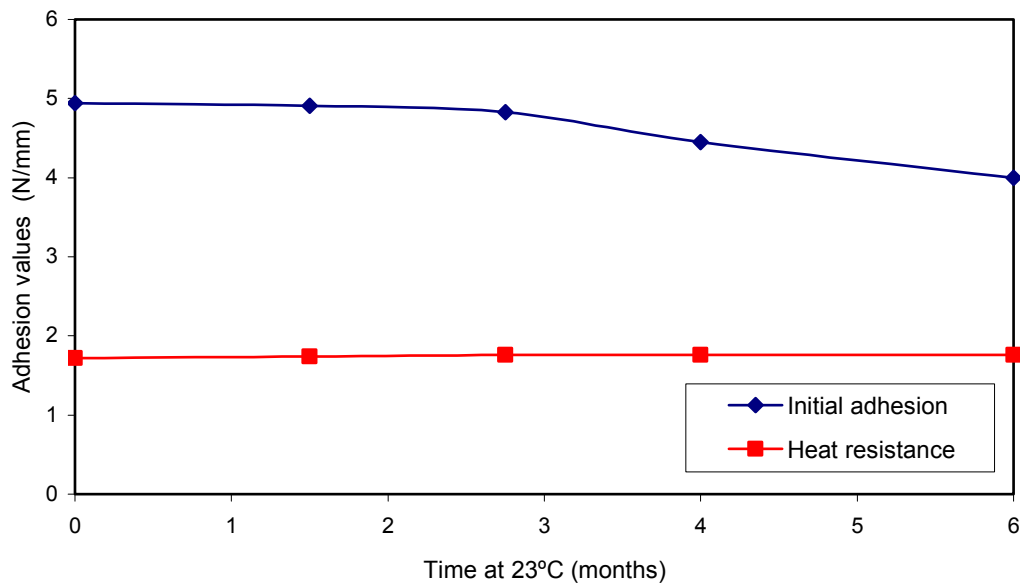


Fig. 3.- Stability of the adhesive values of Disperbond® range

Lower storage temperatures of the dispersion will allow a longer stability time, whereas higher temperatures will reduce it.

3b.- Stability of the adhesive plus crosslinking agent (Pot life)

The stability of the formulated adhesive has been studied, once 3 % Quidur® 444-20 has been added, during 8 hours (usual working day), and the viscosity and adhesive properties changes have been evaluated. The formulations are those that have been previously mentioned. The results are as follows:

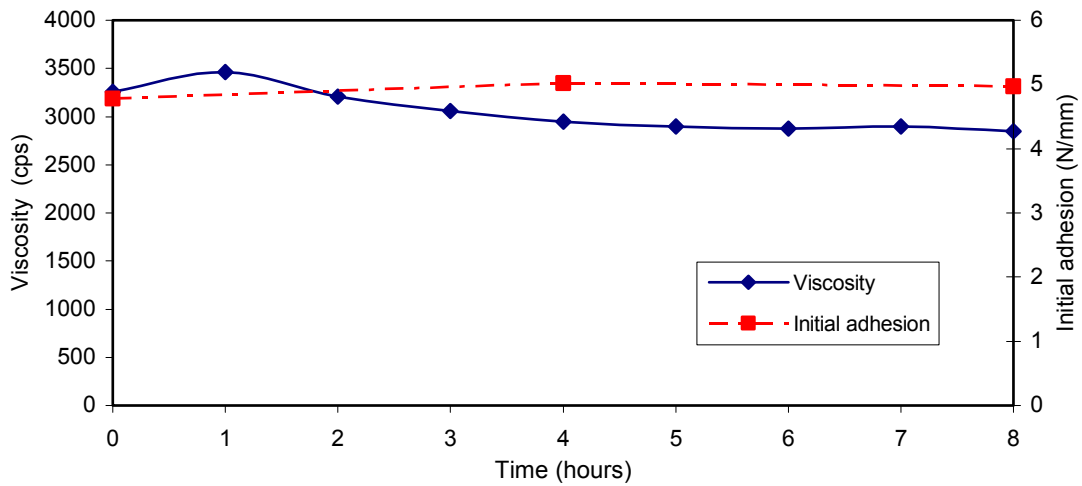


Fig. 4.- Stability of the adhesive formulated with Disperbond® range with 3% Quidur® 444-20

3c.- Stability of the adhesive

The viscosity changes have been evaluated for 2 different viscosity levels. For such evaluation, no crosslinking agent Quidur® 444-20 has been added.

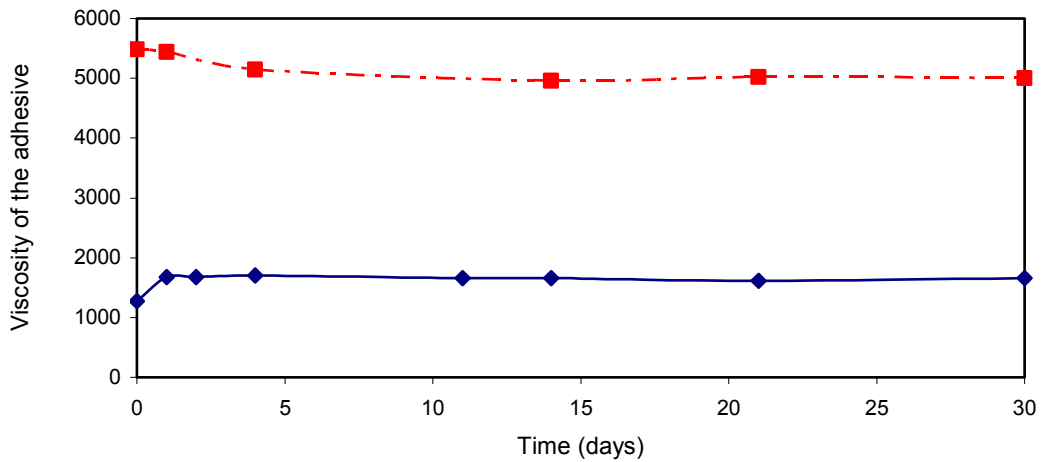


Fig. 5.- Viscosity stability of the adhesive formulated with Disperbond® range

APPLICATIONS OF THE NEW TECHNOLOGY

This new production technology of aqueous polyurethane dispersions is applicable not only to highly crystalline, heat-activated adhesive dispersions, but also to all kinds of polyurethane dispersions, such as those that are used as coatings in a wide variety of markets: flexible textile coatings, paints, varnishes, leather, etc. Since this paper is focused on adhesive dispersions, we will mention the main sectors the new DISPERSION® line is intended for:

- Automotive industry

In the automotive industry, dispersions are used as adhesives for several interior components (panels, etc.). The high initial adhesion of the dispersions produced in accordance with the new technology, together with a high crystallinity, make them especially adequate for such application.

- Furniture industry

In the furniture industry, the dispersions are sprayed on MDF panels, which are then laminated with a decorative film (usually PVC) by membrane press. The low clot content in the emulsions due to the higher consistency of the polyurethane produced by this new process, together with its stability, make them undoubtedly suitable for such application. Besides, their high initial adhesion and crystallisation speed allow perfect bondings without adhesion failures in tensioned zones.

Besides, in these applications, as no light resistance is requested, the use of an aromatic polyurethane is more adequate than an aliphatic polyurethane.

- Shoe industry

In this sector, solvent-based adhesives are mainly used for sole-bonding, but aqueous dispersions can also be used, especially for sports shoes. The high solids contents of DISPERBOND[®] D31W50, together with its adhesion and heat resistance values, makes it especially appropriate for such sector.

CONCLUSION

A new technology for the production of polyurethane aqueous dispersions made out of 100% solids pellets has been presented, which allows:

- The production of a very consistent and highly structured ionomeric polymer, giving dispersions with excellent adhesion values
- Offering to the market polyurethane aromatic dispersions with adhesive characteristics similar to those of the already existing upper range of solvent-based adhesives. At medium term, this may favour the ecological tendency of replacing the solvent based polyurethanes by aqueous dispersions, in the present applications.
- The adhesives maker to produce his own emulsions, with a new field of possibilities not available so far.

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