TRUTH OR MYTH? DO WATER-BORNE ADHESIVES HAVE DIFFICULTIES WITH WATER-RESISTANCE?

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A major share of pressure sensitive adhesives for tapes, labels and films are based on acrylic dispersions.
However, when it comes to applications where water resistance is key - e.g. outdoor applications - some reluctance in the market to use water-borne systems can be found. There is an often-heard statement: "What comes out of water will go into water". Does this statement hold water?
Within this presentation a general understanding about the phenomena, which occur in adhesive films under wet conditions, is outlined. Based on these findings, dispersions were designed and compared to state-of-the-art solvent-borne or UV-hotmelt acrylics.

1. Introduction

1.1 Dispersion Characteristics

An aqueous dispersion consists of a tremendously large number of particles (1 mL of dispersion contains approximately 100 trillions of particles) and, thus, has a huge overall particle surface (see Fig. 1). This surface is stabilized by hydrophilic substances, which prevent coagulation of the dispersion.

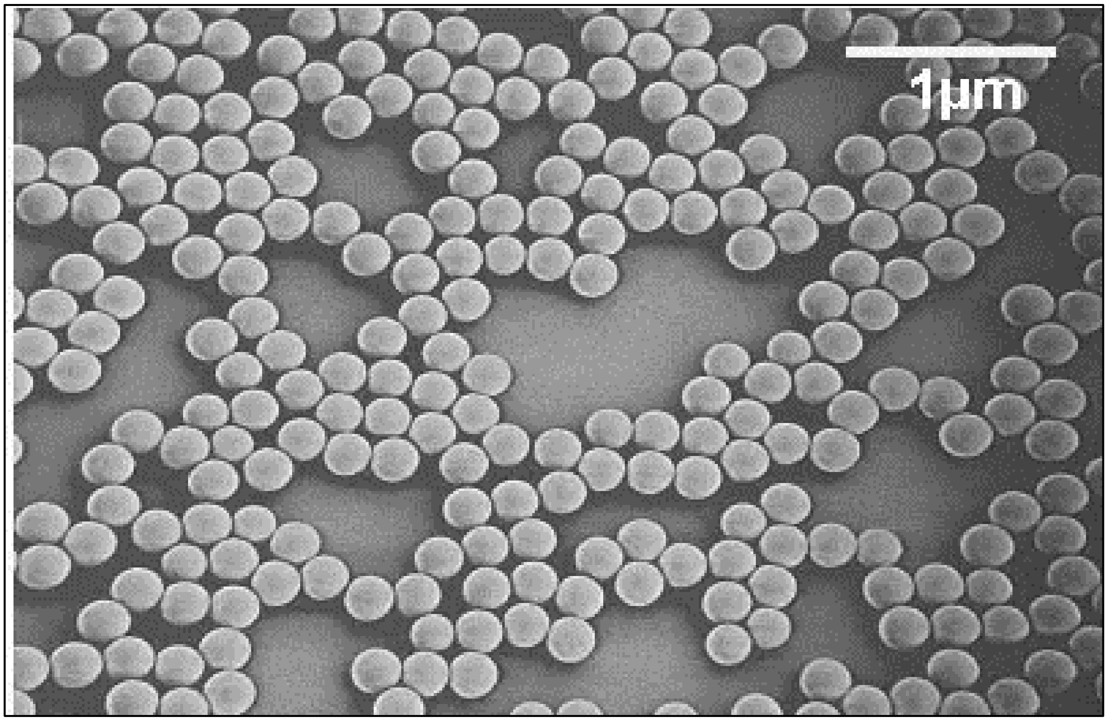

Figure 1. Schematic representation of a dispersion

The final properties of a water-borne adhesive, however, are not given by the dispersion but rather by the film, that forms upon drying. The hydrophilic components remain within the film, which nourishes the suspicion that water-borne adhesives may not withstand water or humidity.

1.2 Water Whitening

A widespread test to assess an adhesives behaviour towards water is to simply immerse an open film in water and see what happens (see Fig. 2):

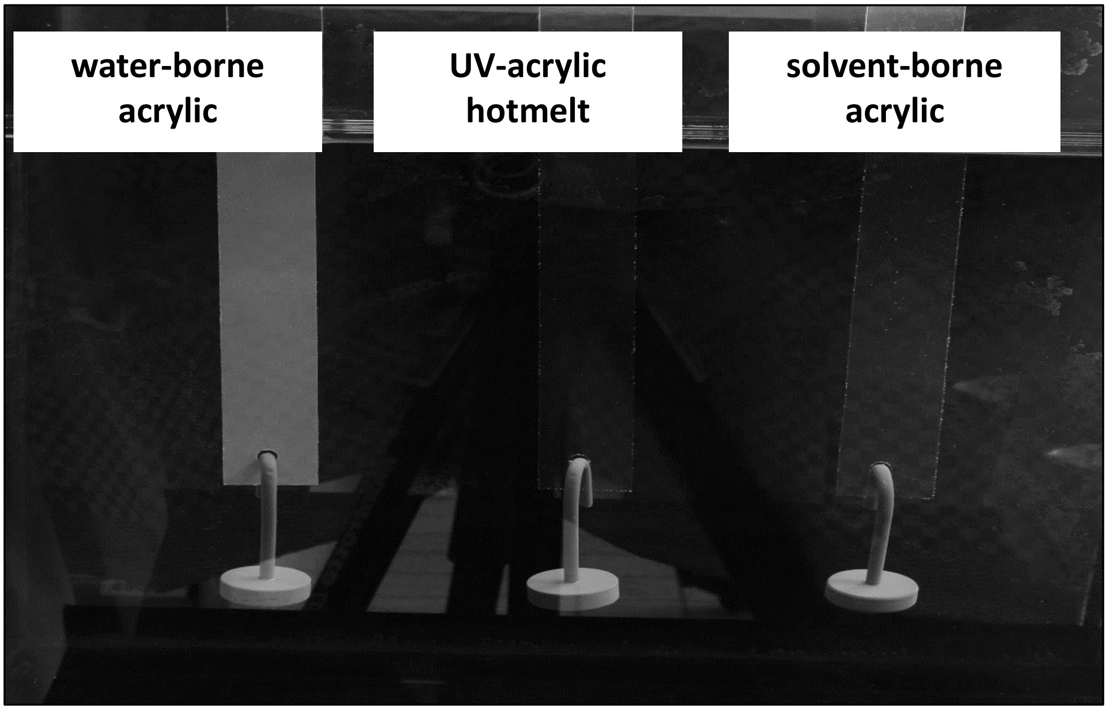

Figure 2. Water whitening of different acrylic-based adhesives after 180 mins

The film, formed from a dispersion is clearly distinguishable from its solvent-borne or hotmelt counterparts by its opaque appearance. However, does this whitening affect the adhesive properties, e.g. its water resistance, or is it simply an optical phenomenon? To answer this question, it is important to know the cause of whitening.

So, let’s have a look on electron microscopic images of dispersion-based films, taken after different periods of time of being immersed into water (see Fig. 3).

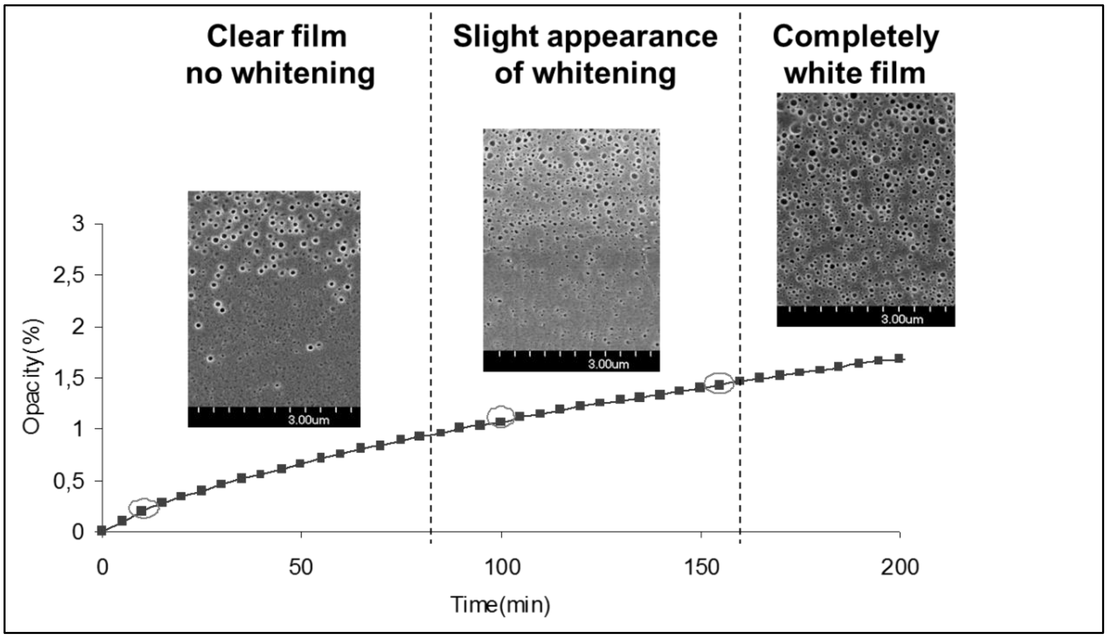

Figure 3. Kinetics of water whitening

The black dots resemble domains (pockets), which were filled with water. These domains increase in number and size after prolonged exposure of the film to water. In other words, the water is not evenly distributed within the film, leading to water-filled pockets with a different refractive index than its surroundings. Once these pockets reach a size comparable to the wavelength of visible light, the whole film becomes opaque.

As already described above, dispersion-based films employ hydrophilic substances. Furthermore, since they are formed out of polymeric particles and not from a homogeneous precursor (such as a polymeric solution or melt), the once particular structure is still visible within the film (see Fig. 4).

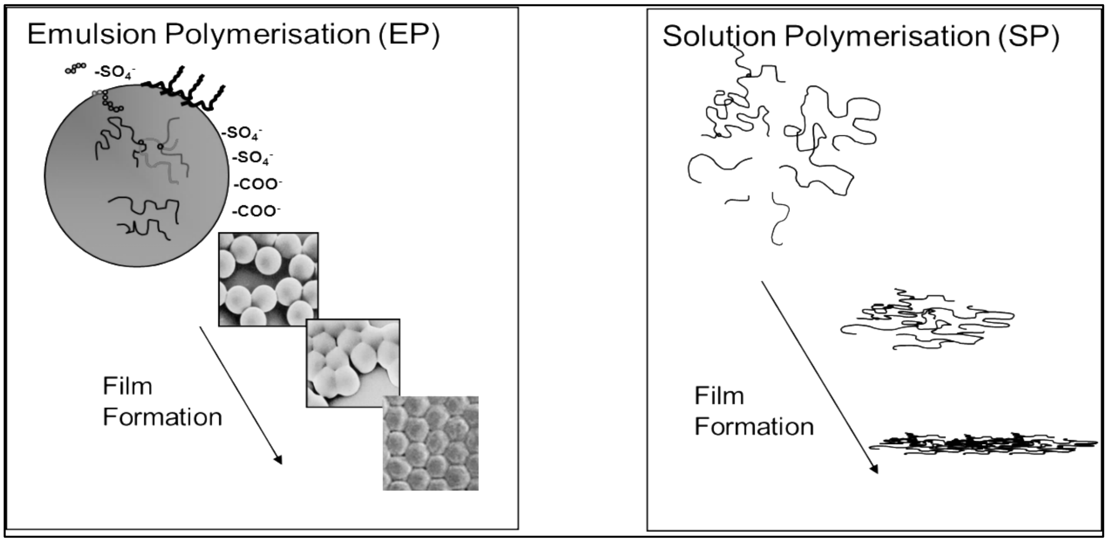

Figure 4. Film formation in emulsions vs.solutions

It is these former particle boundaries where the hydrophilic substances concentrate. Therefore, once water diffuses into the film, it is accumulated preferably in these areas leading to the aforementioned pockets. So, the film heterogeneity is the reason for the irregular distribution of water and, thus, the whitening effect.

The remaining question to answer is if the irregular distribution of water disrupts the adhesive performance. In this regard, it is important to notice that films, derived from solvent- or hotmelt-based acrylics take up water just as dispersion-based films do.

Taken together, all acrylic-based adhesive films, regardless the technology, take on water or humidity. In the case of a film, derived from a dispersion, you can see it. In the case of films, derived from either solution or melt, you cannot.

So, is water whitening a pure optical effect without any implication on the adhesive properties at all? The answer is, as always, it depends: The water pockets could, in principle, cause a mechanical failure of the film and the hydrophilic components may lead to low water resistance, as well.

To circumvent these obstacles, control of film formation and appropriate choice of hydrophilic substances are key in the development of a water-resistant dispersion.

2. Strategies to optimize water resistance of dispersions

2.1. Polymer architecture

Changes in polymer architecture influence the ability of the polymeric chains to interdiffuse beyond particle boundaries. Figure 5 shows images of polymeric films, derived from atomic force microscopy. Soft areas appear dark and stiff areas bright. The particle boundaries, which are covered with hydrophilic components can be seen as thin bright lines.

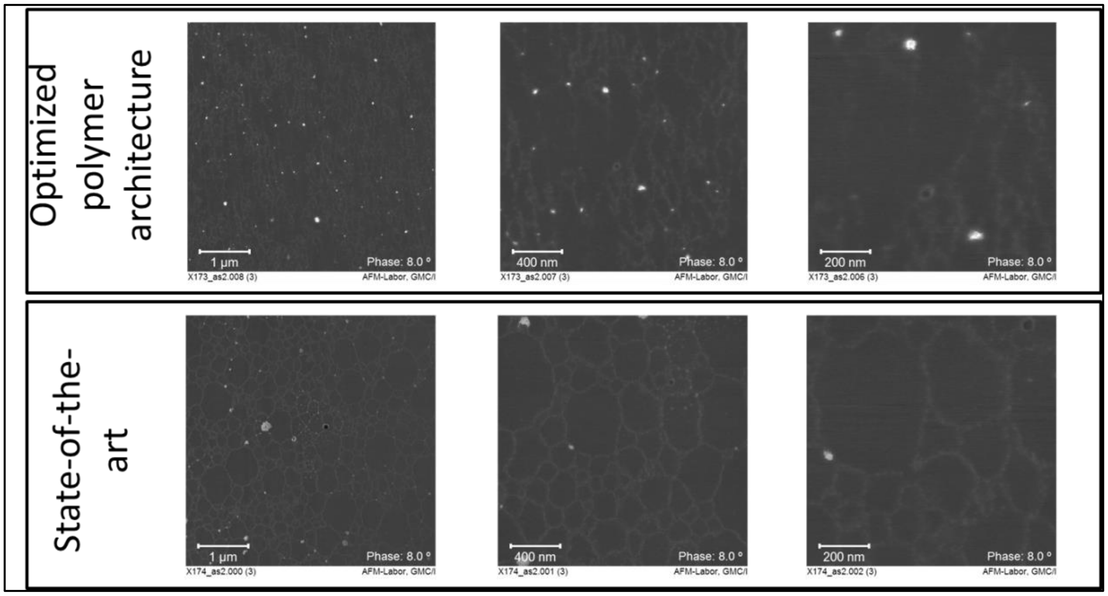

Figure 5. AFM images of different dispersion-based films

Optimizing the polymer architecture can indeed lead to an increased interdiffusion of polymeric chains. It is visible in the upper AFM images where the boundaries are blurred. This interdiffusion strengthens the macroscopic mechanical stability of the film and, thus, increases its cohesion. Beyond that, the size and amount of water pockets, which are formed once water or humidity penetrates the film, can be decreased. This has an overall positive effect on the film's water-resistance.

2.2. Particle size distribution

Quite often, dispersions do not have a single particle size but rather a distribution of different particle sizes. From a theoretical model, it can be concluded, that the difference in size of the particles has an influence on the homogeneity of the film (see Fig. 6).

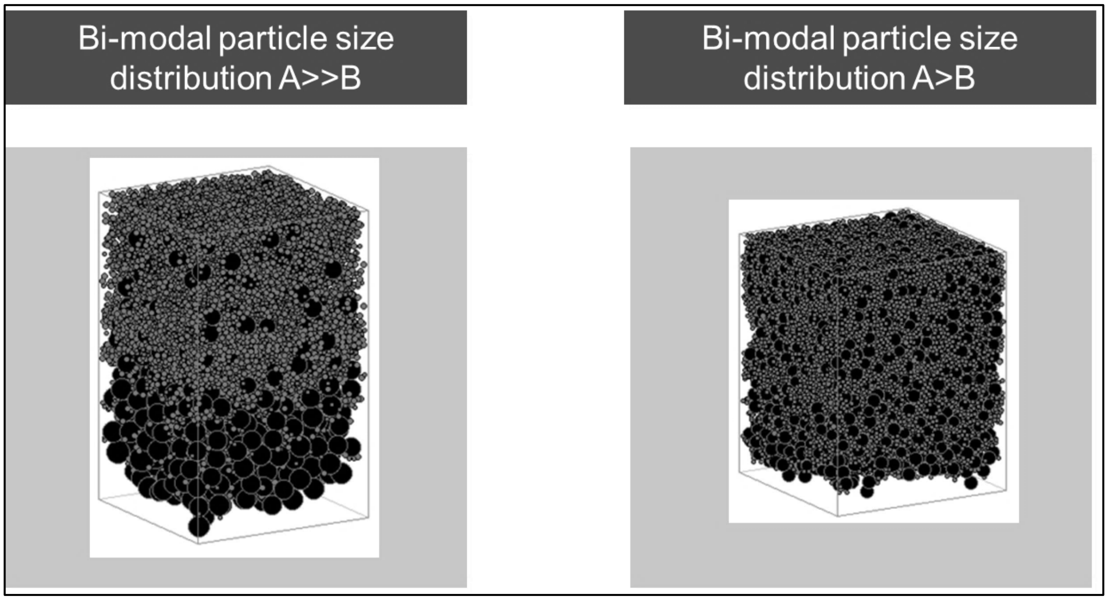

Figure 6. Model of film formation in dependence of its particle size distribution

In the case of bimodal particle size distributions, the film becomes more homogeneously the smaller the difference in size between small and large particles is.
This has an effect on the size of the water pockets, as well (see Fig.7).

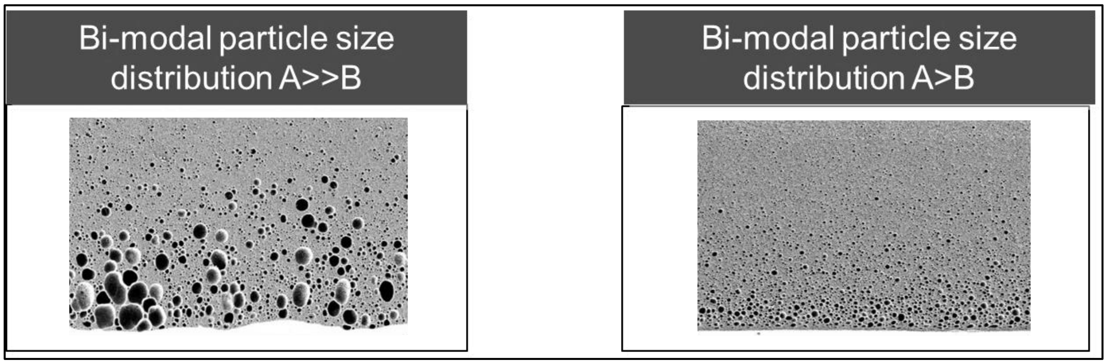

Figure 7. Electron microscopic images of dispersion-based films after immersion in water

Very clearly, the more homogeneously the particles are distributed within the polymeric film, the smaller the water pockets are. This can increase the water resistance of the resulting film.

2.3. Hydrophilic components

Surface-active substances, e.g. surfactants or protective colloids, constitute a major share of the hydrophilic components. It lies within their nature to migrate to any surface available, may it be the surface of the dispersion particles or the surface of any given substrate.
In the following images, confocal laser scanning microscopy (CLSM) was used to monitor the diffusion of water into a dispersion-based film (see Fig. 8). Water is marked by a fluorescence dye and can be identified in the images as bright areas.

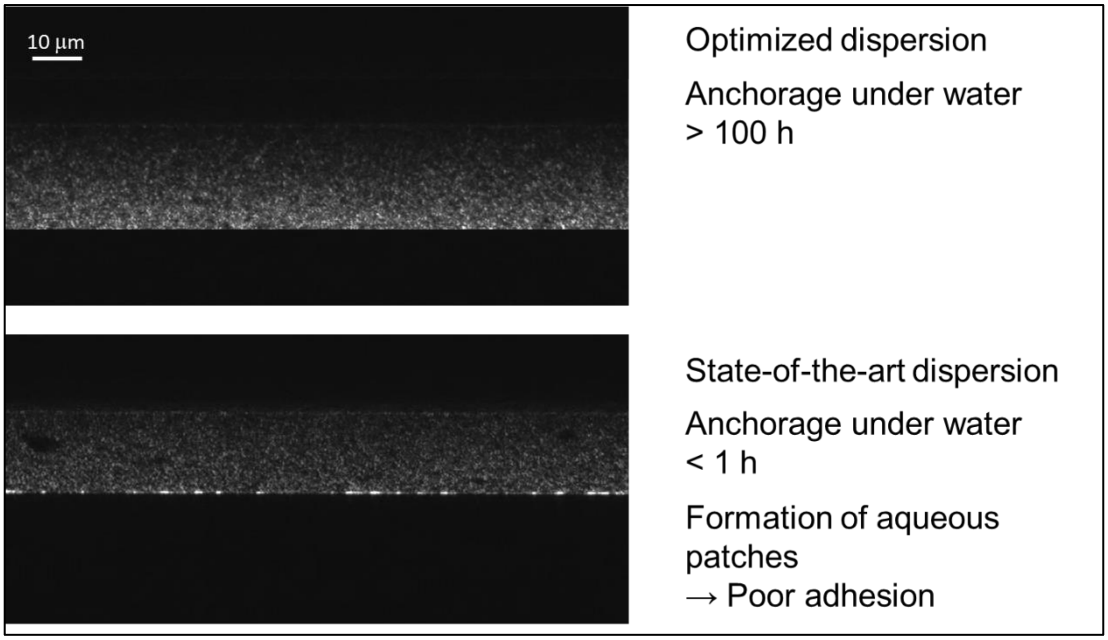

Figure 8. CLSM images of dispersion-based films during immersion in water

In the upper case, the hydrophilic components are optimized in such a way that their tendency to migrate to the substrate (here: glass) is minimized. Once water diffuses into the film, it is distributed rather evenly without being accumulated at the interface between adhesive and substrate. This ensures an optimal anchorage even under adverse conditions.

With a state-of-the art dispersion, accumulation of water at the interface occurs, resulting in rather poor anchorage.

3. Application properties of optimized dispersion-based adhesives

3.1. Field of application

Acrylate-based polymers have long been used to manufacture pressure-sensitive adhesives. Typical applications are adhesive tapes, labels and graphic films.

The technical requirements for a pressure-sensitive adhesive can be very challenging, especially in the area of adhesive tapes.

The requirements for bond durability can vary considerably, depending on the application. This criterion reaches maximum values particularly in the specialty tapes segment. Specialty tapes are often used to create a permanent bond between very different materials, e.g. in the automotive, electronics and construction industries. Therefore, the bond life is determined by the life of the final article, so that a bond is often required to last for years. Furthermore, it is common to use these tapes in outdoor applications, exposing the tape to different environmental conditions with humidity being one of the most critical ones.

Therefore, we conducted comparative application tests of acrylic-based pressure sensitive adhesives derived from either solution, dispersion or UV-hotmelt, which are typically used for specialty tapes.

3.2. Results

All tests were conducted with material that is commercially available. The test stripes were obtained by coating the adhesive with a coating weight of 75 g/m^2 dry on a polyester film with a thickness of 36 µm.

In the case of the UV-hotmelt, a UV-C dose of 40 mJ/cm^2 was applied. The test conditions for shear (e.g. cohesion) and peel (e.g. adhesion) are to be found in the appendix (see Fig. 9).

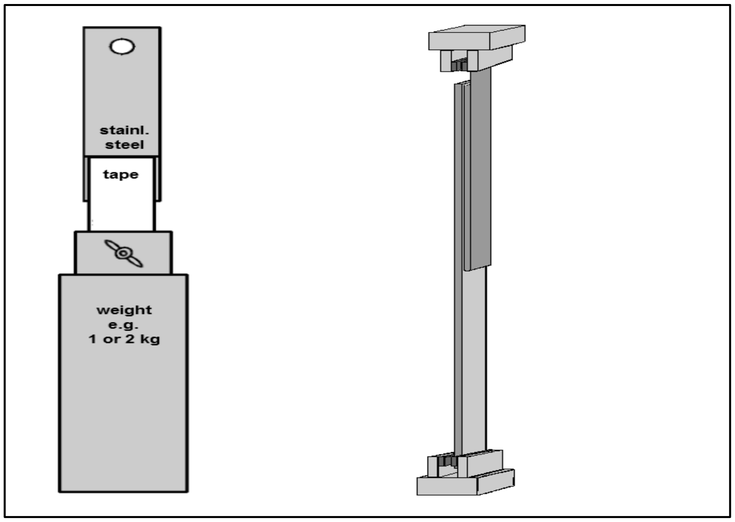

Figure 9. Schematic drawings of shear and peel test set-up

Since it is water resistance, which is the scope of this presentation, these tests were altered accordingly: First, we have immersed the whole set up for the determination of shear in water. Figure 10 shows the comparative results for shear under normal conditions against those for shear under water:
For all adhesive technologies, the decrease in shear once the set-up is immersed in water is significant: The solvent-borne adhesive drops from over 100 hrs shear to less than half an hour, the UV-acrylic from 10 hrs to 75 mins and the dispersion-based to 30 mins. However, the conditions chosen, e.g. an area of 0.5” x 0.5” and a weight of 1 kg may have been too harsh under these circumstances. Therefore, the measurement was repeated with an adhesive area of 1” x 1” and 2 kgs of weight. Under these conditions, the adhesive bond lasted roughly as long as without immersion under water (see Fig. 10, right graph).

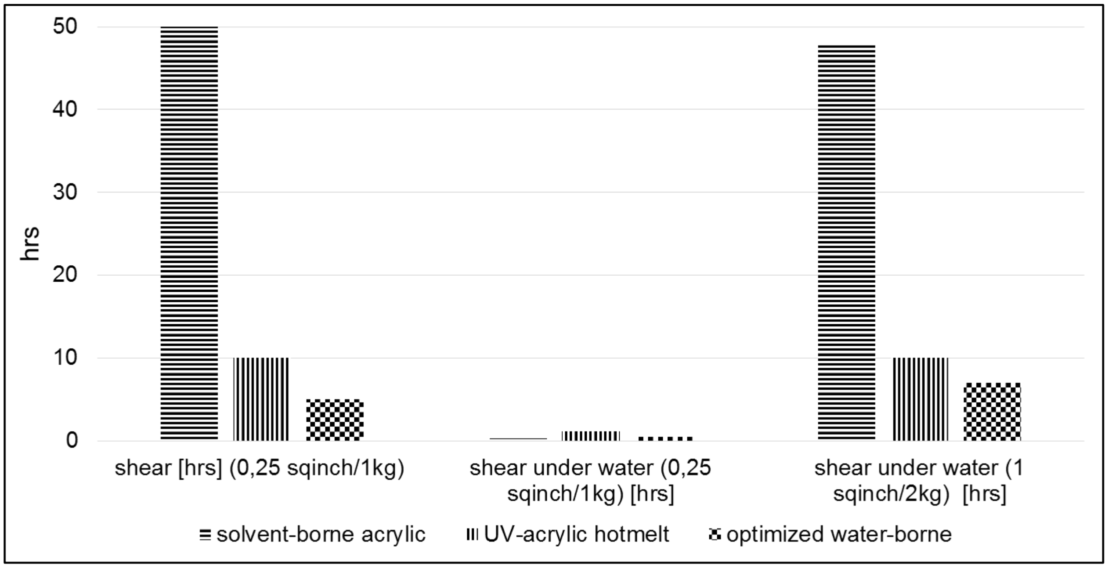

Figure 10. Shear under different conditions

In other words: all tapes, regardless which adhesive technology was applied, suffered under these severe conditions. There is no distinction possible, whether the tape is water-based or not. It simply does not make a difference!

Since it is an unlikely event, that the whole bonded joint is immersed under water, another test protocol was applied: The joint, e.g. the tape bonded to a steel surface, was stored in a climate chamber for a prolonged period of time under humid conditions (65°C at 85% rel. humidity). In regular intervals, a sample was taken out of the chamber and peel, as well as shear, were determined. The whole storage procedure was carried out for 18 weeks at last.

The next figure illustrates the change in peel after this prolonged exposure to humid conditions:

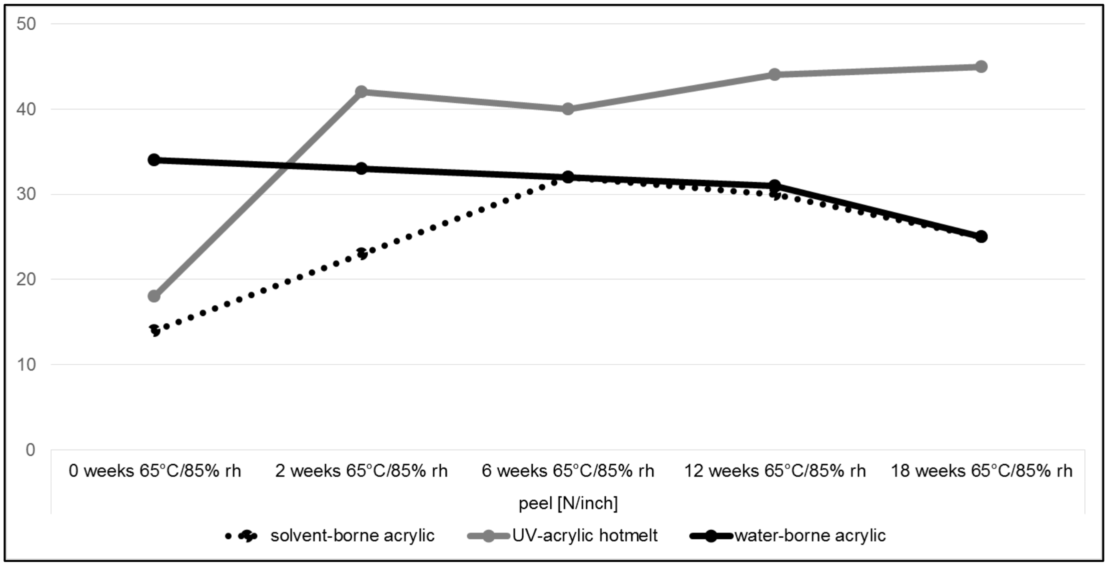

Figure 11. Peel after storage under humid conditions

At the beginning of the test, the dispersion exhibits a higher peel value than its solvent-borne or UV-hotmelt counterparts. This is due to the nature of the commercial sample chosen: The dispersion-based product has been optimized more strongly towards excellent adhesion whereas the solvent-borne acrylic and the UV-hotmelt were specifically designed for high cohesive strength.

Even after prolonged storage, the dispersion remains at high peel values with a slight drop at the end. The solvent-borne sample, as well as the UV-hotmelt start at lower peel values, which increase over prolonged storage. For the UV-hotmelt, this increase continues, whereas the solvent-borne sample shows a slight drop in peel after storage for 18 weeks just like the dispersion.

It is not only the peel, which was determined, but the shear as well (see Fig. 12).

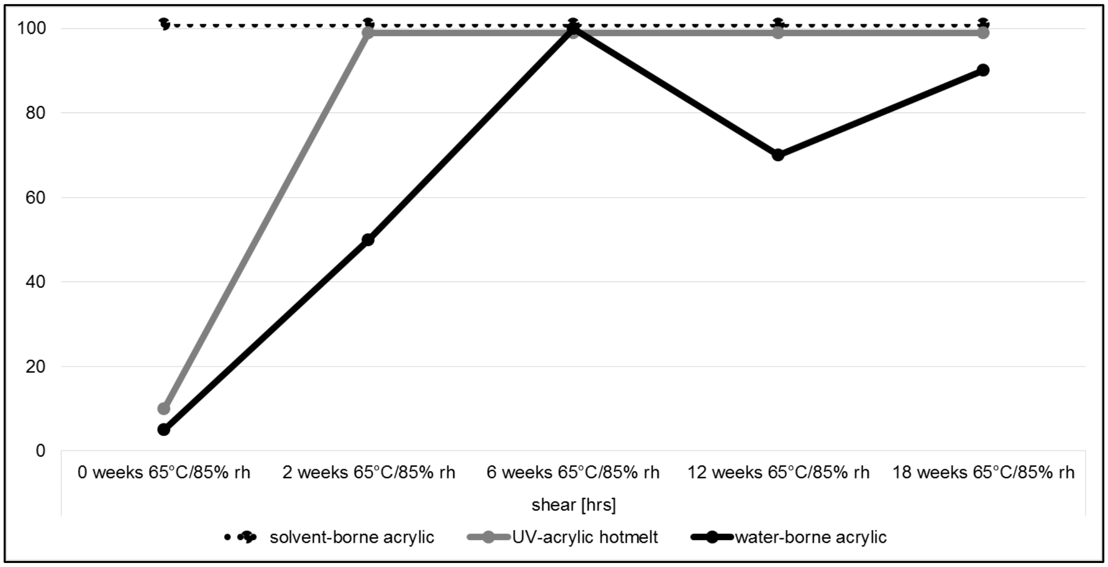

Figure 12. Shear after storage under humid conditions

The original shear values reflect the different application scopes of the samples pretty well: The dispersion is rather adhesive with good shear values. However, when exposed to humid conditions, all samples show very high shear strength, which sometimes exceeds 100 hrs, even under these severe conditions (small area of 0.5” x 0.5” with 1 kg of weight). The dispersion-based tape later oscillates between still excellent shear values of 70 to 90 hours whereas the other tapes stay above 100 hrs. Nevertheless, the dispersion does not lose any performance during the test. To the contrary, the adhesive bond seems to become ever firmer.

The overall pattern of this storage test is the same as of the previous test: There is no weakness of the dispersion-based film when exposed to water or humidity. The changes, which are observed, are always well within the range of the water-free technologies. Performance-wise, the different technologies cannot be distinguished from each other.

4. Conclusion

By carefully controlling the parameters which ensure a film formation as homogeneous as possible and optimizing the inevitable hydrophilic components, a dispersion can be developed that can deal with water as well as the existing water-free technologies. In this case, the effect of water whitening is reduced to a simple optical trick: **Don’t let water whitening fool you!**

5. Appendices

Unless stated otherwise, all tests were performed under normalized climate conditions, e.g. a temperature of 23°C and a relative humidity of 50%.

Adhesion to steel:

The test was conducted with a bond width of 1” and a peel-off speed of 300mm/min after 24h bonding to stainless steel. The measured values were reported in N/inch.

Shear:

The test was conducted with either an adhesive surface of 0.5”x 0.5” on stainless steel and a weight of 1kg or an adhesive surface of 1”x 1” on stainless steel and a weight of 2kg. The static shear was determined, i.e. the time in hours until bond failure.

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