

# Pressure-Sensitive Adhesives ...

... the Underestimated Daily Helps

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Pressure-sensitive adhesives are compounds or, to be more exact, polymeric compounds, that are permanently tacky. Scientific theories abound as to what influences tack and ultimately good adhesion to a wide variety of materials. However, it may be safely said that the strength of a bond is determined by the fine interplay between the polymeric adhesive and the surfaces to be stuck together. The tackier the polymers appear to be, as measured by means of a simple finger test, the softer they usually are, because they are better able to wet the rough surface of the fingertip. On the other hand, high tack often comes at the cost of low cohesion on the part of the polymers.

It is the sheer variety of applications and surfaces, such as the damp glazed tiles in our bathroom example, that stirs the investigative spirit of researchers and developers alike.

Probably, the best known application for pressure-sensitive adhesives in Germany is Tesafilm. In Germany at least, that brand name is now used to describe a whole class of products (comparable with Sellotape in the UK). Nowadays, a large number of other "specialist" products are available to suit every purpose, such as self-adhesive labels that either bond permanently (pricing labels; Fig. 1) or those which must detach cleanly without leaving residues and are often used for glass and porcelain articles (Fig. 2). That the adhesives sometimes cannot be removed cleanly is not necessarily their fault. In such cases, simply the wrong "specialist" was used. After labels, adhesive tapes are the second largest segment. Examples

Imagine you are in the shower early in the morning. Your eyes haven't got used to the glaring bathroom light yet and you fumble around for the towel on the wall. Instead of the hook and your towel, there is only a little, sticky spot on the wall and the towel is lying on the ground. Most people have experienced situations like this before, suffering the inconvenience because a so-called pressure-sensitive adhesive failed.

are the brown adhesive packaging tapes (Fig. 3) or indeed the so-called protective films that every house-builder knows from his new window panes.

Advances in this field were and are still being made rapidly, from the very first self-adhesive materials (simple tree resins) right through to today's acknowledged "specialists" for many different applications. The first permanently sticky articles at the end of the 19th century consisted, from today's viewpoint, of awfully smelly mixtures, such as rubber, turpentine, sprucewood resin, lead oxide and cayenne pepper [1]. Surprisingly, right up until the 1920s, the main applications for such exotic mixtures were medical plasters for wounds (title picture). In Germany, the Hamburg pharmacist P. Beiersdorf was the first to experiment with such rubbers and resins, and soon he too was producing sticking plasters from them. In those days, Beiersdorf advertisements for "Cito" claimed that it was the "adhesive sports tape for cyclists, horseriders and tourists". Cito was the forerunner of today's Hansaplast (German equivalent of UK's Band-aid) [2].

By the early 1970s, there had been a huge rise in the number of pressure-sensitive adhesive products for the most diverse application areas, but natural rubber and resins dissolved in organic solvents such as toluene, xylene and acetone still dominated. One shudders to think how such resins were processed. Solvent contents of up to 70% constitute a major burden on man and the environment when processed without elaborate and thus expensive waste-air and solvent traps. The growing environmental debate that slowly got off the ground in those years ushered in a total rethink on the subject and triggered an intensive search

for more ecologically compatible alternatives.

## Synthetic Pressure-sensitive Adhesives

With the triumphal march of the chemical industry and particularly of plastics, two new classes of synthetic pressure-sensitive adhesive entered the market: hot-melt pressure-sensitive adhesives and aqueous dispersions. The major advantage of hot-melt pressure-sensitive adhesives based on the chemical constituents styrene and isoprene (so-called SIS hotmelts) is that they contain absolutely no solvent while the dispersions have the bonuses of utilizing water, which is ecologically safe.

The SIS systems, which are still used today for adhesive tapes, made enormously high coating speeds possible, relative to both solvent-based polymers and dispersions, since no solvent and no water had to be evaporated. However, the disadvantages of these polymers soon became evident. The high processing temperature of more than 180 °C made direct coating of heat-sensitive materials especially difficult. These yellowed, embrittled and ultimately failed due to rapid ageing through exposure to light and air. It was no accident that packaging adhesive tape was dyed brown ("Havana brown") - on the one hand to act as UV protection and on the other to hide the progressively unsightly adhesive from customers.

Although developed back in the sixties, the pressure-sensitive adhesive dispersions based on acrylates that now dominate the market were initially regarded as outsiders and, like every new idea, had to fight against "received opinion" [3, 4]. It was known that dispersions are environmentally friendly and that the acrylates are very resistant to ageing. However, it

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was nevertheless thought that dispersions with typical water contents of approx. 50% could at best be processed as fast as solvent-based polymers and that it would be impossible to produce a uniform coating on nonpolar (siliconised) films. However, continuous improvements in product properties and, more importantly, simultaneous advances in coating technology gave the dispersions the breakthrough they were waiting for. Production speeds of more than 60 m/min were standard back then; nowadays 80, 150, 300 and more than 600 m/min are feasible. Rapid production of paper labels made it possible for the first time to use them in mass-produced articles, an application that had hitherto been the preserve of rubber. As so often occurs with new technical advances, completely different, unexpected advantages appeared in the course of their development. There was no need to scrap existing coating equipment; it could be refitted to process aqueous dispersions – and at much less cost than was feared.

Despite these advantages and the market success today, it is the disadvantages that inspire further searches for permanent improvements and optimization. Thus, “useless” water, which translates to high transport volume and weight and still restricts coating speed, makes highly concentrated dispersions with solids contents of 70% an even more attractive goal. However, water simply cannot be omitted from production. A look at a greatly magnified picture of an aqueous dispersion reveals the great harmony that sets the hearts of scientists beating faster. One sees spherical, equal-sized beads of dispersion that, as more and more ambient water is removed, approach each other more closely as the dispersion becomes more highly concentrated. The outcome is that the viscosity of dispersions with solids contents greater than 50% increases very swiftly, and this in turn hampers rapid processing. The trick which researchers had to employ to produce highly concentrated dispersions of low viscosity was to selectively generate both large and small particles instead of ones of the same size. The little spheres would then fill the free spaces between the large ones. The viscosity would remain low, even though the solids content was higher (Fig. 4).

A further disadvantage of dispersions is blushing, which occurs in films made from dispersions stored in damp conditions. This is attributed to the emulsifiers and other hydrophilic substances used.

Such films can be used in paper labels, since dulling of the films cannot be seen through the paper. However, in transparent films, e.g. expensive skin creams that have what is called a non-label appearance – i.e. a label that remains virtually invisible – this problem is intolerable.

### ■ The Next Generation

What do users want from the ideal pressure-sensitive adhesive? Of course, it must adhere as well as, if not better than, a conventional solvent-based or pressure-sensitive adhesive dispersion. However, it should not contain organic solvent or water (it should be a 100% system) in order that maximum coating speeds may be ensured (Fig. 5). But it should not yellow in light or air and should remain processable at moderate temperatures, such that even heat-sensitive films can be coated directly. In addition, it should be compatible with

temperatures. Good adhesive properties, though, need high molecular weights.

Now at that time, some work was already being done on radiation-curing systems for a range of different applications, e.g. in paints. UV-active compounds, or so-called photoinitiators, which can initiate polymerisation by means of UV light, were incorporated into conjugated polymeric resins and, after application to a certain surface, were fully polymerised by means of UV light. The problem was that the polymer tended to exude these photoinitiators. This ruled out the use of such a pressure-sensitive adhesive, e.g., on the skin or in contact with food. The crucial step was the use of a copolymerisable photoinitiator, which became chemically bonded to the main polymer chain and could not migrate out of it (Fig. 6).

The result was the ideal “green” adhesive which, logically, complies with the stringent legal provisions governing indi-

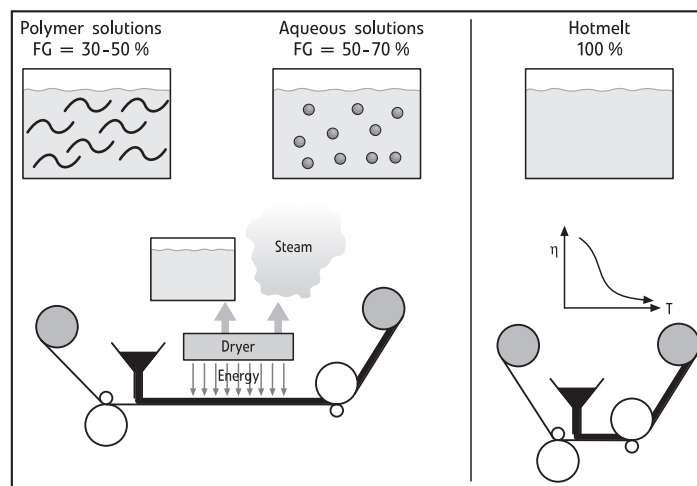


Fig. 5. Possible applications for pressure-sensitive adhesives ( $\eta$  = melt viscosity)

man and the environment, and even so compatible in fact that it can be used in direct food-contact applications.

Until recently, received opinion said “That is impossible!” Yet there is a new generation of pressure-sensitive adhesives that does possess this seemingly extreme combination of properties. A resourceful chemist at BASF had a brain-wave at the end of the 1980s in which he simply united all the divergent strands of thought with each other. He combined the high ageing resistance of the acrylates used in dispersions with the freedom from solvent of the “standard” hotmelts. However, it was also clear that this alone would not suffice, since the viscosity of even a low-molecular, solvent-free polyacrylate is high enough to virtually prevent it from being processed at high tem-

peratures. Furthermore, the dosage of UV radiation to apply affords the adhesive manufacturer a means of deciding on the molecular weight of his adhesive and thus a certain amount of control over the properties that he would like for a specific application. Again, photoinitiators based on benzophenone, unlike many other photoinitiators, also crosslink in the presence of atmospheric oxygen, i.e. there is no need to render the UV irradiation equipment inert. Additionally, the concept of an inbuilt photoinitiator leads to much greater crosslinking yields for the same UV dosage than a photoinitiator that has simply been incorporated.

What are the disadvantages of this seemingly ideal system? To be sure, adhesives manufacturers, who have already been processing standard hotmelts, only

have to fit their coating equipment with UV lamps in order to be able to process such products. They can also directly coat heat-sensitive substrates at much lower temperatures of 120 to 140°C. Equipment used for processing dispersions, however, most probably cannot be refitted for use with hotmelt pressure-sensitive adhesives. These manufacturers wishing to invest in this new technology have no option but to acquire new equipment. In the meanwhile, other manufacturers of adhesives raw materials, following the trend, are now offering radiation-curing systems; some of these are based on widely differing synthetic building blocks, such as epoxides and, usually, incorporated photoinitiators.

In 1998, around 173,000 t of adhesive raw materials (100% solids content) were

processed in Europe, and the trend is growing [5]. Of this approx. 79,000 t are aqueous dispersions and, surprisingly from today's viewpoint, approx. 59,000 t are solvent-borne. These are followed by the standard hotmelt systems at approx. 35,000 t. Measured on this scale, UV-curing systems are currently insignificant. Given the totality of the advantages and the increasing levels of legislation concerning the use of organic solvents, it may be assumed though that this picture will change permanently in the next few years. Whether there will be pressure-sensitive adhesives that replace the present specialists with all-rounders in the next generation is the question still to be answered. If so, never again will the wrong adhesive be used for the bathroom hook mentioned at the start of this article.

#### ■ The Author of this Article

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*Fig. 1. Price labels are bonded permanently to the packaging by means of pressure-sensitive adhesives*

*Fig. 2. Adhesive labels on glass can be removed cleanly without residue*

*Fig. 3. Brown adhesive packaging tapes are among the dominant market applications*

*Fig. 4. The viscosity of a dispersion is a function of the particle size distribution*

*Viskosität = Viscosity; Feststoffgehalt = Solids content*

*Fig. 6. Copolymerisable photoinitiators are chemically bound to the main polymer chain and are not exuded*

*Prinzip der Vernetzung = Principle underlying cross-linking; Fotoinitiator = Photoinitiator; flüssig - un-ernetzt = Liquid - uncrosslinked; fest - vernetzt = Solid - crosslinked; UV-Licht = UV light*