SUMMARY

We have found that a blocked polymeric isocyanate can function as an effective crosslinker for removable acrylic solution adhesives. The blocked isocyanate can be mixed with a hydroxy functional acrylic adhesive to form a one component adhesive with properties very similar to two component adhesives crosslinked with unblocked polymeric isocyanates. The blocked isocyanate has the advantage of having a much longer shelf life which allows practical production of a one package, isocyanate crosslinked, acrylic adhesive. For the end user, this approach eliminates the hazards of measuring and mixing isocyanates and ensures consistent product from drum to drum.

BACKGROUND

Removable pressure sensitive adhesives (PSA) are an important market. Their uses range from removable memo notes, to protective films, to manufacturing aids. When good weatherability and clarity is required, solvent based acrylic PSAs are often used. These materials typically consist of a functionalized acrylic co-polymer crosslinked with a covalent crosslinker such as a polymeric isocyanate. This type of system exhibits good clarity and very stable properties over a long period of time.\(^1\)

Currently, commercial isocyanate crosslinked acrylic PSAs are generally two component systems.\(^2\) Because the crosslinking reaction proceeds at room temperature, the isocyanate must be added and mixed just before the coating operation. After mixing, these materials have a pot life of up to 2 days before they gel and become un-usable — if a catalyst is added the pot life can be considerably shorter. Two part systems have inherent problems such as added labor costs and the exposure of workers to potentially hazardous materials during mixing operations. Also, since the adhesives are typically mixed one drum at a time, each drum is essentially a separate lot. Therefore, quality control can be a problem due to the small lot size and problems resulting from measurement errors or incomplete mixing.
DISCUSSION

Due to these problems, demand exists for a one component system with properties similar to the current two component system. We have found that a convenient way to achieve this is to use a blocked isocyanate instead of a free isocyanate as the added crosslinker. Blocked isocyanates are a well known class of chemicals generally synthesized from a free isocyanate and a molecule with an acidic hydrogen such as polymeric alcohols, ε-caprolactam, or ketoximes (Figure 1).³

![Figure 1. Synthesis of blocked isocyanates](image)

As implied by the reverse arrow in Figure 1, the free isocyanate can be regenerated from the blocked isocyanate by the application of heat. The temperature at which this de-blocking reaction occurs is controlled by the nature of the isocyanate and the blocking agent.³

In order to make a practical, removable PSA using blocked isocyanate crosslinking it is necessary to achieve a reasonable amount of crosslinking (i.e. unblocking) within the time/temperature constraints of the coating oven. This translates into maximum temperatures in the 120 - 150 °C range and times of 1-5 minutes for most facilities. This directed the choice of our crosslinking system to an aromatic isocyanate blocked with methyl ethyl ketone oxime (MEKO). MEKO was chosen because it unblocks at a relatively low temperature, it is easy to synthesize the blocked isocyanate product, and it is volatile enough to evaporate cleanly.³ As many of our customers already use polymeric MDI in their two component removable systems, we chose polymeric MDI (examples include PAPI 27 [Dow] or Mondur MR [Bayer]) as our isocyanate base. When dissolved in a suitable solvent, this isocyanate reacts cleanly and completely with one equivalent of MEKO per isocyanate. The reaction proceeds at room temperature with a mild exotherm; no catalysts or initiators are required (Figure 2). The blocked isocyanate solutions are stable for several months. The reaction is conveniently carried out in methyl ethyl ketone as both the products and reactants are soluble in this solvent.
Figure 2. Synthesis of a blocked polymeric MDI with MEKO.

This material has been shown to effectively crosslink several hydroxy functionalized acrylic copolymers. It also crosslinks hydroxy functionalized vinyl acetate/acylate copolymers. Most of the development work and testing described below was carried out using Gelva Multipolymer Solution (GMS) 1151 from Solutia, Inc. This is a hydroxy functionalized acrylic co-polymer designed for isocyanate crosslinking.

TESTING

The most difficult aspect of testing these materials is determining the level of crosslinking obtained using a given crosslinker level and set of cure conditions. Traditionally, crosslinking in acrylic PSAs is indirectly measured by the shear strength (shear time to failure), but this test is very unreliable in this case because the material fails adhesively in the shear test. We settled on using the 180° peel test⁴ as a measure of crosslinking. As expected, we have found that the peel strength decreases as the assumed level of crosslinking increases. In many instances this appears to be a linear dependence.

Studies of the experimental one package system show that the extent of crosslinking (as inferred by peel strength) is extremely dependent on the cure temperature. This is can be seen in peel values shown in the graph in Figure 3. The uncrosslinked material has a peel value of about 1000 g/cm when cured at 90 °C for 5 minutes. The peel value of the crosslinked material drops as the cure temperature is increased. Full cure is achieved by heating the one package adhesive for at 120 °C for 5 minutes. Full cure is defined as the level of cure as achieved by the two package system comprised of the same base adhesive crosslinked with an equivalent amount of unblocked isocyanate.
Figure 3. Peel vs. cure temperature at 5 minutes of cure. Notice that the un-crosslinked sample (×) had very high peel, while the sample with an equivalent amount of un-blocked isocyanate (▲) had peel similar to the blocked sample fully cured at 120 °C.

Figure 3 shows that at 120 °C, 5 minutes is required to reach full cure. This is much too long to be practical for most coating lines. The limiting factor is the slow unblocking reaction, but this reaction can be greatly speeded up by increasing the cure temperature. Figure 4 shows the results of an experiment designed to emulate a coating oven with a maximum temperature of 140 °C. The samples were cast, allowed to sit in the fume hood for 2 minutes, placed in a 90 °C oven for 1 minute, and then transferred to a 140 °C oven for varying lengths of time. Figure 4 shows that full cure can be achieved after 90 seconds at 140 °C, and that further curing does not decrease the peel value.
A key property of this type of isocyanate crosslinking is that the peel does not build with time. Using fully cured samples, we have also shown that the peel does not build significantly when samples are subjected to several types of aging conditions. Samples were aged under various conditions and the peel values were periodically checked. The results, shown in Figure 5, do not reveal a clear trend in peel values indicating that the peel does not build appreciably over time. The samples aged in under high humidity conditions have a significantly higher peel than the other types of aging. The reason for this difference is not clear.
Since the crosslinker level controls the peel of the final product, an experimental design was carried out to map out the limits of this system. The effect of coatweight was also measured in this simple main effects study. The samples were fully cured by heating at 120 °C for 5 minutes prior to testing.

The experimental design confirmed the expectation that peel is dependent mostly on the crosslinker level, while coatweight has a limited effect. The dependence is nearly linear between 0.5% and 1.5% of crosslinker. Data taken at a crosslinker level of 2% (not shown) did not lower the peel significantly relative to the 1.5% sample, indicating that the crosslinking sites are basically saturated at a crosslinker level of 1.5%.

![Contour plot of the effect of crosslinker level and coatweight on peel level for the experimental one package system.](image)

CONCLUSION

Potential disadvantages of the one package system include a requirement for increased cure time and temperatures and the introduction of MEKO into the manufacturing environment. Since the ability to access the increased cure time/temperature is wholly dependent on the coating equipment used, some coaters may not be able to reach the temperatures required to achieve a practical line speed. This is an unavoidable problem of working with blocked isocyanates. Most of the MEKO blocking agent will be released in the oven during the curing step, although a trace amount will probably be left in the adhesive after cure. Assuming 90% of the blocked isocyanate is de-blocked
during the curing step, the MEKO content of the adhesive after curing will be approximately 0.05% w/w. Most of this extremely small amount of MEKO will be sequestered in residual blocked isocyanate, free MEKO will not be released by the adhesive until it is heated above 90 °C. Therefore, the risk of release of appreciable amounts of MEKO in an uncontrolled environment is small.

This system has distinct advantages over the two package system. The biggest advantage is that the blocked isocyanate is formulated during manufacture. This increases product consistency, increases plant safety and reduces labor costs. Also, because the unblocking reaction occurs only upon heating, isocyanate crosslinking can be achieved without the hazards of measuring or mixing isocyanates. Finally, this is a "drop in" system. Assuming the coater can achieve high enough temperatures, there are no additional capital costs associated with using blocked isocyanate systems.
LITERATURE CITED

4 Solutia test method A-010, based on PSTC-1.