Reliable Laminating interdependency inks/adhesive

working for you.
DIC is the **market leader** in Japan on Performance Lamination Adhesives and for adhesives research.

Sun Chemical is a vital part of DIC’s portfolio, accounting for around half of Group Sales – currently focused on Inks and coatings.

Sun’s reputation for High Performance Lamination inks and unrivalled Technical Support are well known in Europe. We know and understand the needs of our customers in this market.

Since DIC manufactures its own polymers used in both inks and adhesives, Sun is the **only** global ink supplier offering an integrated ink and adhesive system with **full control over the Chemistry**.

For our customers, this synergy means:
Stronger Bonds, Faster curing, greater chemical resistance and greater confidence than ever before.
In order to get the highest mechanical performance of the laminate a certain level of entanglement between the different layers, constituting the structure, should be obtained.

Let’s see in details how each individual layer performs and interaction with the others and possible improvements.

You mention entanglement here but almost completely ignore it for the rest of the talk.
There is no single theory to explain adhesion completely.

*Frequently, adhesion is a synergistic combination of the penetration, adsorption, electrical and diffusion forces.*

**Mechanical interlock theory:** suggest that the main mechanism of adhesion is penetration of one component into irregularities of the other surface. (This occurs on porous substrates such as paper and board), but it can occur at certain levels also with inks-adhesive (as showed later), leaving less amount of adhesive to bond on the second substrate.

**Adsorption theory:** the attractive forces between surfaces are interpreted in terms of chemisorbed and physical sorbed of the atomic and molecular species at the interface. Another term of this theory is **wetting theory** – *wetting is a prerequisite for forming adhesive boundary layer* (Van der Waals forces determine the wetting).

**Diffusion theory:** attributes the adhesion to the inter-molecular entanglements. Adhesion due to diffusion theory gives the strongest bonding when some degree of chemical compatibility is available – the more the better.

**Chemical adhesion theory:** is occurring by chemical bonds like ionic and covalent and metallic bonds.
Normally the most used theory for best performance in a laminate is the wetting theory (surface treatment of the interface). Although popular, it is usually wrong.

I would like to explain it by an example considering the following structure:

\[
\text{PET/ PET met/PE}
\]

Where the PET met in between has only one side chemical or corona treated (the one where the metal has been deposited).

In this case even though the plain side of PET met to be laminate with PET has a naturally high level of surface energy (42-44 dynes/cm) if it is not given extra treatment during the process, it will give a failure or low performance when the adhesive will be completely chemically cured.

This is why the treatment in line is not just increasing surface energy but also creating some functional groups and modifying the molecular structure of PET (on micro level) to get the level of entanglement/intermingling which provide the best performance.

This is also valid for chemical treated substrate, which are normally recommended to not be treated in line, to avoid destroying the coating, even if the process increases surface energy.
One of the most common mode of failure in the laminate is delamination at inks layer level even if the anchorage of the inks itself to the substrate has been proven by tape test method.

The reason of this mode of failure has to be evaluated at level of inks-adhesive layers interaction.

As general overview we can say that two level of interactions characterized the interaction inks-adhesive:

- Chemical interaction between some inks functional group and adhesive functional group
- Physical interaction (lay down/porosity/solubility etc)

While the chemical interaction has mainly an influence on the mechanical performance of the laminate (adhesion, thermal and chemical resistance of the laminate), the physical interaction has influence on two parallel aspects:

- Wettability of the adhesive over the inks and resulting final aspect of the laminate (spots, appearance of laminate)
- Mechanical performance of the laminate (adhesion, thermal and chemical resistance of the laminate)
The complexity of the ink layer is normally forgiven...in fact ink layer is normally a composition of different inks layers (colors + backing white) to obtain the desired design and graphics and additionally different inks can interact between each other in function of:

- the type of printing process (flexo or gravure)
- The type of chemistry (NC, NC-PU, PU, PVB, PVC)
- Solvent release

Furthermore the process of lamination could vary in function of:

- Lamination process (in line or our of line vs inks)
- Type of adhesive’s technology use (Solvent based; solvent free; water based)
While some aspect of the interaction between inks and adhesive are well known such us:

1. **Ink smearing issue (Physical interaction)**
   
   This is normally a physical phenomenon of inks re-dissolution which take place mainly with solvent free adhesive and specifically low molecular weight –OH component due to high compatibility and slow curing process.

2. **Low mechanical performance (chemical interaction)**

   This is a specific problem of loosing of mechanical performance (Bond, thermal and chemical resistance) of the adhesive itself due to a shift of the stoichiometric ratio between the –NCO part and –OH part of the adhesive for a presence of additional, fast reactive, -OH groups from the inks (solvent retention).

3. **Wettability (spots) physical interaction**

   This is a problem related to the roughness of the inks layer which has to be “compensate” by adequate coating weight of the adhesive to get uniform lay down and perfect final appearance.

*Most of them are still unknown and/or unclear*

**SunChemical** is the unique player on the market having internally a full control and knowledge of the chemistry of both the layers (inks-adhesive) and being able to formulate systems in order to get the best performance when combined.

**SunChemical** is dedicating specifically resources to fully and better understand all the mechanism which are regulating the interaction between inks/adhesive layer to provide to customer a solution for easy and better lamination process.
Ink smearing issue (physical interaction)

- Certain Solvent free Adhesives can re dissolve certain inks
- Most commonly seen on flexo designs, designs with no backing white, and process printed areas
- Generally caused by the Adhesive Hardener, (MW of PEG)
  - Ink Type also plays a part – NC more prone to attack
    - Reducing coating weight normally helps
    - Ensure INK & ADHESIVE compatibility
A new backing white inks was tested by customer different in chemistry then process colors.
During the preliminary trials, using the same operative condition in term of lamination process (same coating weight, same solvent free adhesive, same machine setting) it was observed a different of wettability with a lot of spots and worse adhesive wetting when new backing white was used.
So we started from this for our investigation.
Laminate section analysis by SEM

Same inks chemistry color + backing white

Different inks chemistry color + backing white
Backing white surface analysis by SEM & AFM

Same inks chemistry color + backing white

Different inks chemistry color + backing white
Backing white surface analysis by SEM & AFM

Same inks chemistry color + backing white
Different inks chemistry color + backing white
In order to obtain the best appearance of the final laminate, adhesive need to cover completely the roughness of the inks to avoid visual defect.

The SEM & AFM images of the white un-laminated backside and the cross-section of the laminates show significant differences between the samples. The new white un-laminated backside is rougher and show over the whole area more bigger particles than the std backing white.

Looking at the cross-section of the samples a two clear layers of the ink and adhesive are observed on sample 1 while on the other only one layer is visible. This indicates that on sample with new backing white adhesive, applied at same coating weight, penetrate more covering only partially the inks roughness giving problem of spots and additionally low mechanical propriety (less amount of adhesive on top of inks to bond with second substrate).

The problem of course could be overcome by increasing the amount of adhesive applied or working on inks itself to decrease its roughness, improving the lay down having smoother surface less porous.
Chemical interaction

While the problem of adhesive’s performance lost, by reaction of isocyanate from adhesive with hydroxyl groups from the alcohols (solvent retention), is well known, we analyzed also the influence of the reactive groups constituting the inks formulation/chemistry to be able to optimize the package inks/adhesive.

Average first component MW of solvent based adhesive: 7000-25000 dalton
Average first component MW of solvent free adhesive: 2000-6000 dalton

In general term we can say that the functional groups available from inks are limited affecting the performance of solvent based adhesive (with some exception) due to the limited level of solubility due to high MW of adhesive.

Different scenario instead occurs with solvent free adhesive where due to the LMW and high “mobility” (low green tack) the level of solubility into the inks is much higher and presence of reactive groups can influence the final performance.
Questions?

Thank you

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