Shrink Sleeve Flexo Inks

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ABSTRACT

The shrink sleeve market is growing annually at a very rapid rate up to 15%. The shrink film producers are constantly making changes in their products to make them cheaper, more environmentally friendly and more efficient. Thus, the shrink film market for flexography and rotogravure printing offers large inventory of various ink chemistries for all kinds of films available. The purpose of this project was to develop a product that would print on different shrink sleeve films and exhibit excellent printability and end use properties such as adhesion, block resistance, shrinking ability with no change in optical properties, such as haze, and/or transparency.

INTRODUCTION

Packages are changing and developing constantly as the brand owners try to gain market share. High quality graphics is expected as purchasing decisions are made mostly at the point of sale. Clear polymeric labels are increasingly desired, since they provide a no-label look to decorated glass and plastic containers. Paper labels block the visibility of the container and/or the contents in the container. Clear labels enhance the visual aesthetics of the container, and therefore the product, and are growing much faster than paper labels in the package decoration market as consumer product companies are continuously trying to upgrade the appearance of their products on store shelves. Flexible packaging has been used to replace folding cartons (stand-up pouches), cans (flexible retort pouches, rigid plastics (drink pouches) and corrugated (shrink wraps). Narrow-web flexography, a technology adopted by flexo label printers to do printing on paper-board, flexible packaging, is often used to print shrink sleeves. Shrink-sleeve applications can be very challenging, yet profitable. Technology continues to change, and ink and coating systems get more advanced and specialized every day.

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The shrink-sleeve market is growing at a very rapid rate. This was reported by by recent Flexographic Technical Association's market research study. It showed that approximately 77 percent of the targeted audience manufactures print wrappers, 75 percent make pouches, 74 percent fabricate bags, 69 percent make shrink-sleeve labels and 68 percent produce full body shrink sleeves (Anon, 2005). Some authors indicate annual growth up to 15%. Customers are more interested in heat-shrink sleeves for branding their products (Peters, 2005). The PVC shrink sleeve is the latest development for use in non-returnable lightweight glass bottle decoration, and decoration of various plastic bottles. Tension management is a critical function when printing on any shrinkable substrate on flexographic presses. Utilizing chill rolls provides an excellent method to keep the web cool and prevent premature shrinkage (Ryback, 2005). The ink systems required by the shrinkable substrates must have the same ability to shrink at the same rate as the substrates. Several film materials are available such as polyvinyl chloride (PVC), oriented polystyrene OPS, glycol-modified polyethylene terephthalate (PETG). Films for shrink sleeve packages may be also formed from polymers and copolymers of olefin monomers containing from 2 to about 12 carbon atoms such as ethylene, propylene, 1-butene, or blends of mixtures of such polymers and copolymers. Nitrogen and oxygen containing monomers such as amide, ester, and/or ethylene/vinyl acetate are also frequently used.

Shrink sleeves may be single or a multilayer film having a first layer, which is an outer layer, comprising an ionomer, and a second layer consisting of any of polymers such as: ethylene/vinyl acetate copolymer, vinylidene chloride, polyethylene homopolymer, polypropylene homopolymer, and ethylene/alpha-olefin copolymer, polyvinyl chloride, polyamide, polyester, and/or polystyrene. There are also multilayer films having at least three layers, including layers consisting of one of the following: ethylene/vinyl acetate copolymer, vinylidene chloride, polyethylene homopolymer, polypropylene homopolymer, and ethylene/alpha-olefin copolymer, polyvinyl chloride, polyamide, polyester, and/or polystyrene (Williams et al., 2003). The multilayer film structures may be coextruded or laminated.

PVC as a sleeve material is easy to control during the shrink process and it is also cost-effective, has many good properties such as good scuff resistance, ease of printing, but is not environmentally friendly because of presence of chlorine atoms in the polymer macromolecule. PETG is also known as glycolised polyester. The "G" represents glycol modifiers, which are incorporated to reduce brittleness and premature aging that occur with unmodified amorphous polyethylene terephthalate. PETG films are amorphous, meaning the polymer molecules are not aligned or ordered within the material. Another material, polyethylene terephthalate (PET) offers a higher percentage of shrink, which is an advantage in some application. Oriented polystyrene (OPS) represents a very common alternative to PVC shrink films in Asia and Europe, but at this point it is not readily available in the USA. OPS is slightly higher priced than PVC film but is more recyclable and has a greater shrink percentage.

The shrinkability of the film can be described using the degree of "total free shrink" of the film. Preferably, the film has a total free shrink at 185° F of about 25 %, before the shrinking step is carried out. Very often the film before shrinking has a total free shrink from about 70 to 110%. The shrinkability of the films used in the packages provides a tight fit around a container. The sleeve has to shrink by up to 62% to fit the bottles and/or tubes (Anon, 2004). A tight fit is achieved using a conventional hot air shrink system.

High quality graphics calls for high quality inks. Today's inks must withstand the heat used for retorting (in flexible packaging) or shrinking (in labels). Film manufacturers are coming up with new solutions, which forces ink formulators to create new ink systems or try to formulate universal inks, compatible with most of the shrinkable films on the market. Specialized UV free-radical systems are now available for shrink-sleeve and thin-film applications with quite interesting results (Kilbo, 2004). The two main UV curing systems are based upon free radical and cationic chemistries. The new UV system provides fast free radical cure speeds and high adhesion to allow the inks to fuse with the substrate immediately upon cure (Williams, 2005).

Solvent-based inks for flexographic printing on non-porous substrates, such as polyethylene and polypropylene, are well established. Those formulated with a pigment, a fast-evaporating organic solvent and a resinous binder represent the state-of-the-art in packaging printing. They produce high quality full-color images with excellent adhesion and abrasion-resistance even when the package is stored in a freezer for extended period of time. A common resin in the solvent based flexo packaging inks are the reaction products of a polymerized fatty acids (dimer acids), diamines or mixture of diamines, and a terminating monocarboxylic acid. These polymerized fatty acid-based polyamide resins, suitable for use in flexographic inks, are widely used. The organic solvent in these inks is typically a blend rich in a lower alcohol, for example, ethanol, n-propanol, or isopropanol, since these alcohols are good solvents for the resinous binder and evaporate rapidly after printing. Flexographic packaging inks may also contain lesser amounts of a lower aliphatic ester, such as ethyl acetate and propyl acetate.

Film manufacturers are constantly coming up with new solutions for improved film products, which forces ink formulators to create new ink systems or try to formulate universal inks, compatible with most of the shrinkable films on the market, and this was also the aim of present work.

EXPERIMENTAL

Ink Formulation

Inks were formulated in laboratory scale, using a Morehouse Cowles CM-100 Lab dissolver equipped with a chambered shaft. The metal vessel was filled to 2/3 of the volume with the milling media (0.7 mm ceramic beads from Morehouse Cowles) and the colored pigment dispersion was milled for 15 minutes. White inks were dispersed with Morehouse Cowles CM-100 Lab dissolver equipped with high sheer blade.

Film Substrates

Polyvinylchloride (PVC), oriented polystyrene (OPS), and glycol-modified polyethylene terephthalate (PETG) substrates were obtained from various plastic suppliers.

Flexo Printing

A flexo Hand proofer was used to print formulated inks. Aniloxes with 200-360 lpi with 7-5 BCMs were used for printing. Coating weights were 0.7 lbs/ ream to 1.0 lbs/ream, depending on the color.

Printed Structures

Various reverse printed combinations were printed:

Substrate / Colored ink
Substrate /White ink
Substrate / Colored ink / White ink
Substrate / Colored ink / White ink / White ink
Substrate /Colored ink / Colored ink / White ink / White ink

End-use Properties of Printed Films

The following end-use properties were tested before and after the ink was printed and sleeve was shrunken:

- Tape adhesion (610 Scotch tape)
- Block resistance (42˚C @ 10 PSI for 24hrs)
- Abrasion resistance (nail scratch)
- Coefficient of friction (static and kinetic)
- Ice-water crinkle resistance
- Shrinking performed using shrinking frame (shrinkage rate adjustable)
- Shrink ability (No haziness after shrinking)

RESULTS AND DISCUSSION

Several different ink systems were preliminarily tested for performance on different shrink sleeve films. The ink has to shrink at the same rate as the substrate, it needs to stay transparent, has to be flexible enough, and it must not cause blocking after shrinking. The first ink that was formulated for use at OPS, PVC and PETG was a nitrocellulose (NC) based one with formulation range given in **Table 1**. Slightly different amounts of individual components were used for different ink colors. Solvent used in formulation was alcohol /ester mixture 80/20 by weight.

Table 1: Formula of nitrocellulose ink

Component	Amount [wt %]
Solvent	40-65
NC/urethane	10-15
Pigment	8-40
Wax package	1-3

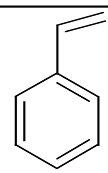
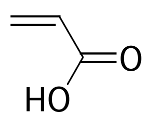
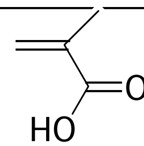
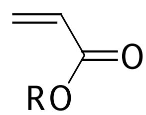
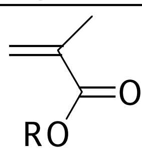
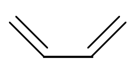
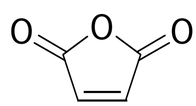
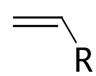
The problem with the NC ink formulation was that it adhered perfectly to PVC, but the adhesion was not 100% on OPS and PETG. Therefore, new ink chemistries were explored. Acrylic ink system showed the greatest potential from all the products tested for shrink sleeve application. We were concerned about blocking and film forming properties of future ink films.

Table 2: Properties of acrylic copolymers

Contributing Monomer	Properties
Methyl Methacrylates (MMA)	Block resistance, abrasion resistance, hardness, gloss retention, fast dry speed, solvent resistant
Ethyl Methacrylates (EMA)	Clear softer films, pigment wetting, fast solvent release, block resistance, tolerance to alcohols
Butyl Methacrylates (BMA)	Softer films than MMA, excellent adhesion
Styrene	Block resistance, hardness, initial high gloss, poor gloss retention, fast dry speed
Short chain acrylates and Methacrylates	Flexibility, stain, rub resistance, adhesion
Acrylic/Methacrylic Acid	Adhesion, resolubility, hardness, solvent and grease resistance
Long chain acrylates and methacrylates	Flexibility, adhesion, intact

Blocking and film forming properties are closely related to polymer transition temperatures. Most of the polymers have two transition temperatures: T_g, the glass transition temperature, corresponding to the amorphous region and T_m, the melting temperature corresponding the crystalline region of the polymer. T_m is a sharp transition called first order transition and T_g is a continuous transition, also known as a second order transition. T_g is temperature at which the non-crystalline portion of the polymer is transformed from a tough rubbery material to a brittle glass-like material. Transition temperatures of polymers are crucial for choosing polymeric resins suitable for particular ink formulation. Glass transition temperatures for resin systems of our interest were in the region of 55-65ºC with the aim of obtaining a harder ink films. Acrylic resins chosen for this project were thermoplastic, thermally stable up to 177º-230ºC, very flexible, with excellent abrasion resistance. Also, they produced transparent films and were resistant to discoloration after heating. Acrylic polymers can be made of different monomers, responsible for finely tuned properties of inks, as listed in the **Table2**. Chemical structures of different monomers for these acrylic copolymers manufacture are shown in the **Table 3.**

Table 3: Chemical structures of monomers for acrylic copolymers

 Styrene	 Acrylic Acid	 Methacrylic Acid	 Acrylates
 Methacrylates	 Butadiene	 Maleic Anhydride	 Alpha-Olefin

Relatively low molecular weight methacrylates showed the highest potential for shrink sleeve inks, because of their high pigment wetting ability, solubility in ethyl alcohol, and formation of clear flexible ink film properties, without displaying adverse consequences such as label lifting or hazing.

Ink formulation was performed with respect to different shrink film chemistries. The selection of solvent was the crucial task. The choice of solvent involves many factors, including evaporation rate, solution viscosity, the effectiveness of a solvent depending on its ability to adequately dissolve one material while leaving other materials unaffected as well as environmental and health concerns. Solvent action depends on the two characteristics of solvent, Hildebrand's solubility parameter delta (δ) (**Table 4**), and hydrogen bonding capacity, expressed as hydrogen bonding index gamma γ. The Hildebrand's solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization. When two solvents are blended, the delta δ and gamma γ values for resultant mixtures fall on straight line connecting the points representing the individual components. The Hildebrand value of a solvent mixture can be determined by averaging the Hildebrand values of the individual solvents by volume.

Table 4: Values of Hildebrant solubility parameters for selected solvents

Solvent	**Hildebrant solubility parameter [calories.cm^{-3}]**
Methyl ethyl ketone	9.27
Cellosolve® acetate	9.60
Butyl Cellosolve®	10.24
Cellosolve®	11.88
n-Propyl alcohol	11.97
Ethyl alcohol	12.92

Solvent compatibility with substrates was also an issue: While PVC and PETG withstand ester/alcohol solvents, OPS film was easily distorted by ester presence. Therefore, ink formulation should not contain more than 20% of ester. Also, it was found that improper amounts of acetates might result in a pearlescent cast on some shrink films. Finally, it was believed that a balanced combination of acrylic/cellulose acetate propionate system does result in successful ink formulation having key attributes required by diverse shrink wrap markets. A map of solubility of methacrylate resins in solvents of various solubility parameters is illustrated in **Figure 1**.

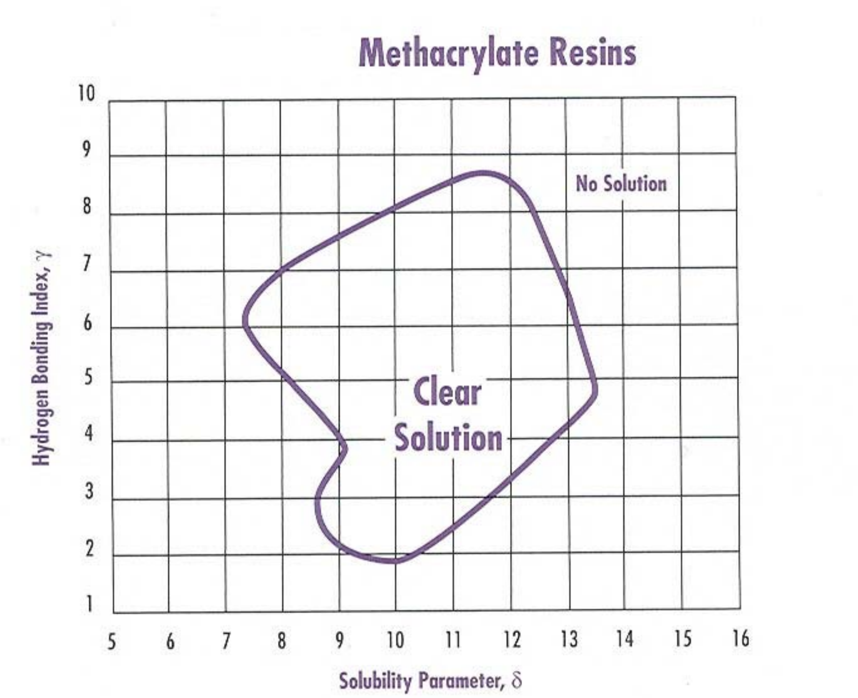


Figure 1: Map of solubili\ty of methacrylate resins (Annon, 2002)

Table 5: Wax Additives for Solvent-based Systems

Melting Point [˚C]			
160		High COF	
150		Sandability	
130	Anti-blocking		
110	**X**		Scratch resistance
90			**X**
70		Low COF	
50	◄		►
	Lower	Polarity ◄	Higher

Wax additives that were used in shrink sleeve ink systems were chosen according to the rules presented in **Table 5**. The wax package had to provide ink with good slip and excellent scratch resistance. Additionally, the wax package had to inhibit ink's blocking. However, based on **Table 5**, it was challenging to choose a single wax giving anti-blocking properties as well as proper scratch resistance. Therefore, at least two different waxes had to be used in ink formulations to bring these necessary properties. The final formula rangfe of the acrylic ink is given in **Table 6**.

Table 6: Formula of acrylic ink

Component	**Amount [wt %]**
Solvent mixture	40-65
Methacrylate Resin	8-22
Pigment	8-35
Additives	2-6
Wax package	1-4

The ink was printed on all substrates with coating weight of 0.7 lbs/ream to 1.0 lbs/ream depending on color. Viscosities of individual inks are given in **Table 7**.

Table 7: Viscosity of individual inks measured with Zahn # 3 cup

Ink Color	**Viscosity [cP]**
Solvent Mixture	56
Yellow	90
Magenta	140
Cyan	90
Black	95
White	250

All acrylic inks showed better performance than nitrocellulose inks on all tested substrates, having perfect tape adhesion, scratch and block resistance, expected static and kinetic coefficient of friction, and passed ice water crinkle test.

CONCLUSION

Solvent based flexo inks were formulated for selected films (OPS, PETG, and PVC). Acrylic formulations had better performance than nitrocellulose inks, exhibiting expected properties on all three most widely used substrates. Acrylic ink formulations met the specified target properties such as adequate shrinking ability without clouding/haziness after shrinking, excellent tape adhesion before and after shrink. They were scratch resistant, exhibited perfect ice-water crinkle and block resistance and met specifications for coefficient of friction.

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