Study of textile pigments transfer print with Nano-form (PVC/DEHP) composites

E. Allam[1] ,R. Azzam[1] and A.Abd El-Moniem [2]

[1] Textile Printing, Dyeing and Finishing Department, Faculty of applied arts, Helwan University, [2] Consultant of textile printing & finishing, CEO of SPI Company
ceo@spi-eg.com

Abstract: Transfer print is one of textile printing techniques which enable small printing shops to do work without much equipments and workers, traditional method deals with sublimation transfer technique which suites only synthetic fibers (polyester fabrics), white or pale shade backgrounds while pigments transfer of (PVC/DEHP) composites can applied for all types of fabrics either dark or white backgrounds depending on the highly adhesion power of the investigated composites and the reforming ability of the elastomeric polymer composite.
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Key Words: PVC poly vinyl chloride, DEHP diethyl hexyl phthalate

1.Introduction

Nano processing means any technology done on a nanometer or (10^{-9}) meter scale, at least in one dimension of the particle, Nano size can synthesis by to ways, condensation method by building atom by atom forming nano size particles, dividing method by dividing large particles forming nano size particles, each one has several synthesis processing.

Application of new transfer pigment printing inks depending on nano science is a must in modern textile industry to achieve such characteristics and gaining new customers, also application of nano science in printing inks leads to increase the productivity and quality of printing which simulate the new machines and equipments.

Polyvinylchloride (PVC) has a linear structure similar to polyethylene but with a chlorine atom replacing a hydrogen atom on alternate carbon atoms. PVC itself is hard and rigid but the addition of phthalate esters as plasticizers makes it soft and pliable and ideal for gloves, photographic dishes and tubing. Polyvinylchloride is generally transparent with a bluish tint.

Plasticizer is a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability. (1)

Titanium dioxide is a widely used white pigment because of its brightness. It can also oxidize oxygen or organic materials; therefore, it is added to paints, cements, inks, or other products for sterilizing, deodorizing and anti-fouling properties and when incorporated into outdoor building materials can substantially reduce concentrations of airborne pollutants. (2)

2. Experimental

1-Chemicals and materials

1-1-PVC used in a wide range of applications. Paste PVC finds its principal end use in the home, where it is used to make flooring and wall coverings .The other half is spread among consumer goods, artificial leather, industrial and automotive applications, coated fabrics, gloves, sealants, conveyor belts and foams, medium molecular weight.

Supplied by INEOS ChlorVinyls, Sweden *www.ineos.com*

1-2- DEHP the main plasticizer for EPVC to improve flexibility of PVC resin, Supplied by LG Chem, Ltd. Korea *www.lgchem.com*

1-3- ESO Refined Soybean Oil can be used for making Plasticizers and Epoxidized Oils, to maintain the plasticity of PVC and as a stabilizer for increasing the stability in PVC and Pesticides, used in Surface Coating Industries such as Paints, Varnishes, Printing Ink and related products, Supplied by Gujart ambuja exports limited. India *www.ambujgroup.com*

1-4- **$CaCO_3$** supplied by El-Eyman co. Egypt

1-5- Calcium zinc supplied by Triveni chemicals, India *www.trivenichemical.com/stabilizer-1.html*

1-6- Titanium dioxide DuPont has been a pioneer in titanium dioxide technology for the coatings industry and ranks 1st among titanium dioxide manufacturers in product quality, customer service, and production capacity, supplied by DuPont *www2.dupont.co*

2- Substrates

2-1 -100% knit red cotton fabric 150gm/m^2

2-2- 100% knit red polyester fabric 130gm/m^2

2-3-100% knit white cotton fabric 145gm/m^2

Red cotton samples were scoured; half bleached and dyed with reactive vinyl sulfonyl dyestuff at 60C^o, washed and dried, white cotton samples were scoured; one bath bleached, washed and dried, poly

ester red samples scoured and dyed with red disperse dyestuff, washed and dried.
(All fabrics supplied by Martex clothing company, Egypt)

3-Tools and equipments

3-1- Low speed mixer

www.anatol.com

3-2 -Laboratory high-speed disperser SAII-3

www.sowerchina.com

3-3- Wet Nano Milling machine

www.millgroup.co

3-4-Manul printing machine

6-colors printing machine

www.lancergroup.com

3-5- Flash-cure digital infra-red unit:

Anatol Infrared Panel Flash is an affordable and simple solution that is especially a great option for a startup textile printing shop.

www.anatol.com

3-5- Convert-belt infra-red digital dryer

The Solutions series dryers are perfect for textile printers looking for an efficient and affordable complement to their output demands.
www.anatol.com

3-6- Heat-transfer digital pressing machine:

Fully digital temperature control with automatic digital timer Super-portable light machine weight – 103 lbs Extreme high pressure capability with hardened high-strength pivot points

www.lancergroup.com

4- Measuring instruments

Infra-red digital thermometer:

Infra-red thermometer allows to easily determining the surface temperature of difficult to reach targets, or objects that are moving or fragile.

www.professionalequipment.com

5- Methodology

5-1-Mixing process

Suggested recipes from PVC, plasticizer and additives were mixed with low speed hand mixer for 5 minutes, then dispersed with t high speed disperser for about1minute, the temperature during mixing and dispersing process must be below 60C^{o}, all samples were kept for 1 hour before testing or further processing.

5-2-Milling process

The dispersed samples were subjected to wet nano mill two times under cooling condition to keep the temperature below 60 C^{o}; the milled samples were kept for about 1hour before testing or subjected to further processing.

5-3-Printing and coating

The printable pastes were printed or coated upon the substrates which described as mention through screen with mesh count 61/cm using square shape 70Duorometer squeegee using manual screen printing machine, two layers were applied ,flash for 2 seconds in between two layers to dry 1st layer using infra-red flash cure unit.

5-4-Curing and fixation

All coated or printed fabrics were flashed for 2seconds after printing or finishing process was finished then fixed at 150C^{o}for 1minuite using infra-red convert belt dryer.

5-5-Heat transferring technique

The mirror image design were printed onto the coated paper using recommended mesh count (mesh count 61/cm), dry the printed color at 80C^{o} for 10 seconds using hot air infra-red convert-belt dryer, repeat the drying step for each color, transfer the finished paper upon the textile fabric using heat transfer machine at temperature 170C^{o} for 5 seconds, medium pressure (2-3P) was recommended, slowly cold peal the paper from the fabric.

5-6-preparing and testing laboratory

All samples were prepared and tested at SPI production and QC laboratory while productivity study was carried out at Garo print- shop.

www.spi-eg.com

6-Practical procedures

1--Study of pigment transfer print of (PVC/DEHP) composite

Not: 2%of CaZn, 2%of ESO and 10%of CaCO3 were added to all recipes for thermal stability.

1-1-Transfer print with (PVC/DEHP/30%TiO_2) composite

Thirty percent TiO_2 were added to the 5 ratios (2, 3, 4, 5, and 6) of (PVC/DEHP) composite as reported in table(1), the 5 samples were mixed, milled and printed upon coated transfer paper with print methodology as mention, the printed papers were

dried at80 C° for 10seconds using infra-red convert belt dryer, the dried paper were applied onto dark cotton fabric using heat transfer machine for 5seconds at 170C°cold peal technique was applied, results were observed and reported in table 1.

1-2 Transfer print with clear (PVC/DEHP) composite

Five ratios (2, 3, 4, 5, and 6) of (PVC/DEHP) composite as reported in table 22, the 5 samples were mixed, milled and printed upon coated transfer paper with transfer print methodology as mention, the printed papers were dried at80 C° for 10seconds using infra-red convert belt dryer, the dried paper were applied onto white or light fabric using heat transfer machine for 5seconds at 170C°cold peal technique was applied, results were observed and reported in table 2.

2- Effect of flash-cure additive on gelation time of (PVC/ DEHP) composite

1%, 2%and 3% flash -cure additive were added to each one of the 5 ratios (2, 3, 4, 5, and 6) of (PVC/DEHP) composite, the 15 prepared samples were mixed, dispersed and milled as mention, the samples were printed upon white cotton fabric all printed samples were adjusted to flash-cure unit, the gelation time calculated for each recipe, results reported in table 3 and figure 1.

3-Effect of glossy, matt and designed paper on coating film of (PVC/ DEHP) composite

Four ratios (2, 3, 4, and 5) of (PVC/DEHP) composite were prepared and printed on white or red cotton fabric with mixing and coating methodology as mention, the coated samples were subjected to heat transfer press using glossy paper upon the coating area for 5 seconds at temperature 170C° with pressure about 3P, last step was repeated with matt and designed paper, results was observed and reported in table 4.

4- Studying the (PVC/ DEHP) composite as (foil and flock) paper and metallic powder adhesive

The 5 ratios (2, 3, 4, 5, and 6) of (PVC/DEHP) composite were prepared and printed upon white cotton fabric, the printed samples semi cured at 80C°, with methodology as mention, foil and flock paper was applied onto the cotton fabric using heat transfer press for 5 seconds at 170C°for foil and 190C° for flock, cold peal technique was applied 10results were obtained and reported in table 5.

(15% of metallic powders) were added to the prepared pastes of ratios (2, 3, and 4,) of (PVC/DEHP) composite, (15% of flakes) were added to the prepared pastes of ratios (2, 3, and 4,) of (PVC/DEHP) composite, the metallic powder or metallic flaks were mixed well into the milled paste then printed upon white cotton fabric with methodology as mention, 6 results were obtained and reported in table 5.

3. Results and Discussion

Transfer print: is transferring the printed film from paper into the fabric under certain condition which described as mention. Oil-based transfer suitable for all types of fabrics which not affecting by heat as transferring process done at temperature between 170C° in case of flat transferring film, while 200C° applied in case of puff transfer.

Oil-base transferring film applied either on white or dark fabric; in flat oil-base transfer the paper must be coated paper and applied onto the fabric by cold-peal technique, while in puff transfer technique the paper must be uncoated and applied onto the fabric by hot-split technique.

Cold peal technique: the printed paper pressed using heat transfer machine at temperature 170C° under pressure about 3pars, the paper split away from the fabric after 30seconds.

Hot split technique: the printed paper pressed using heat transfer machine at temperature 195C° and pressure about 3 pars, the paper split away from the fabric immediately.

In multi-color printing, drying in between colors at 80C°, and then all colors drying at same temperature, higher temperature must be avoided as it has bad affect the transferring process.

1-1-Transfer print with (PVC/DEHP/30%TiO_2) composite

Table 1 Study the transfer print of (PVC/DEHP/30%TiO_2) composite

Ratio	2	3	4	5
PVC%	20	30	40	50
DEHP %	80	70	60	50
Silicon %resin	2	-	-	-
Transfer result	Bad result	Good transferring	Excellent transferring	Excellent transferring

1-2 Transfer print with clear (PVC/DEHP) composite

Table 2 Study the transfer print of clear (PVC/DEHP) composite

Ratio	2	3	4	5
PVC%	20	30	40	50
DEHP %	80	70	60	50
Silicon %resin	4	3	2	2
Size after	good result	excellent transferring	Excellent transferring	Excellent transferring

Tables 1 and 2 showing that: the suitable combination ratios for color, clear and white inks were ratios 3, 4 and 5 while ratio 5 preferred for puff transfer while ratio 3 preferred for clear backup.

Comparison between sublimation transfer and oil based composite transfer

Oil-based composite transfer clear, white or colored suitable for both natural and synthetic fabric depending on its highly adhesion power to the applied fabrics, while sublimation transfer suitable only for synthetic fabric.

Oil-based composite transfer can applied onto white or dark backgrounds as white composite can applied as backup for much hiding power while sublimation transfer can apply only onto white or pale shade backgrounds.

Oil-based composite transfer can applied either flat transfer or puff-transfer while sublimation transfer can apply only as flat transfer.

Both oil-based composite transfer and sublimation transfer can processed either by screen printing or by offset printing, in case of offset printing composite was applied by screen onto the offset printed area as a backup (mask) only as the ink composite itself not suitable for offset printing.

2- Effect of flash-cure additive on gelation time of (PVC/ DEHP) composite

Oil-based film never dry by air even after long time as the gelation of the film doesn't occurred without heating, 80 C^o is the gelation temperature for most PVC/DEHP ratios,

150 C^o is the fixation temperature at which the printed film strongly fixed at the printed substrate.

In transfer print only gelation was needed as the fixation applying by heat transfer machine , if drying temperature is raised more than 80 C^o the film partially fixed onto the paper and showing bad transferring result.

Table 3 Effect of flash cure additive on curing time of PVC/DEHP composite

Ratio	2	3	4	5	6
PVC%	20	30	40	50	60
DEHP %	80	70	60	50	40
0% F.A/sec	8	6	4	4	3
1%F.A/sec	6	4	3	3	2
2%F.A/sec	4	2	2	2	2
3%F.A/sec	3	2	2	2	2

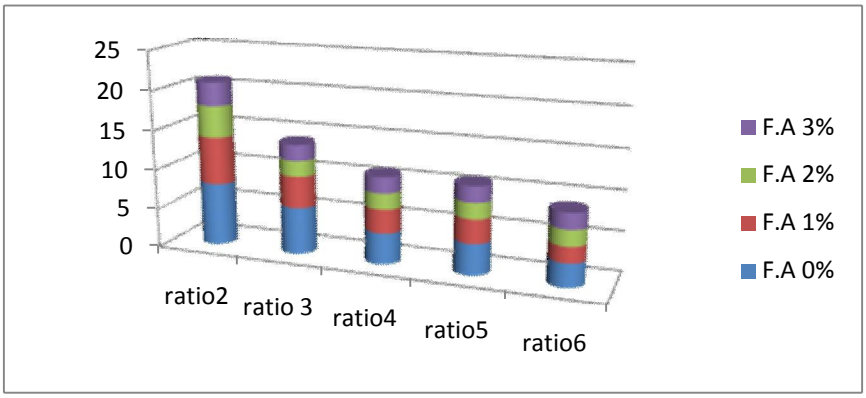

Figure 1 Effect of flash cure additive on curing time of PVC/DEHP composite

Table 3 and figure 1 showing that: the drying of oil-base printed film affected by the addition of flash-additive which reduce the drying time of printed film and increase the productivity either in direct or transfer print, the percentage of flash-additive inversely proportional to the drying time , the suitable percentage was 3% flash –additive which minimize the drying time to 2seconds , also notice that the drying time decreased as the PVC percentage increased as showmen in ratios 2,3,4, and 5 .

3-Effect of glossy, matt and designed paper on transferring film of (PVC/ DEHP) composite

As oil-base film can thermally reformed so it was affected by high temperature (melt) and dried again by cooling, such effects as mirror glossy, matt appearance and animal skin or other effects were applied.

Semi-crystalline thermoplastics become less brittle above 'Tg. If a plastic with otherwise desirable properties has too high a Tg, it can often be lowered by adding a relatively low molecular weight plasticizer to the melt before forming and cooling. Thermoplastics can go through melting/freezing cycles repeatedly and the fact that they can be reshaped upon reheating gives them their name. This quality makes thermoplastics recyclable. [3, 4]

Table 4 Effect of matt, glossy and designed paper on printed area with oil based composite.

Ratio	2	3	4	5
PVC%	20	30	40	50
DEHP %	80	70	60	50
Matt paper	No effect	Matt film	Matt film	Matt film
Glossy paper	Little glossy	Glossy film	Mirror effect	Mirror effect
Designed paper	No effect	Skin effect	Skin effect	Skin effect

Table 4 showing that the final printed film affected easily when pressed by using gloss paper to achieve mirror effect, matt paper to achieve matte effect, fish skin designed paper to achieve fish skin effect, snake pre designed paper to achieve snake skin effect on printing area, all these effects applied by heat transfer machine, the predesigned paper considered to be stamps, ratios 4and 5 sowing a clear result as it contain higher PVC percentage while ratio 2 shows no or little effect.

The final fixed and printed film thermally affected by predesigned paper achieving newer and wonderful effects either on all printed area or in specific area changing the future of printing inks, water-based inks cannot thermally affected by any way after fixation.

4- Transfer study of (PVC/ DEHP) composite as flock, foil and metallic (powder, flaks) adhesive

Flexible PVC/DEHP composites have a great adhesion power which can be used as bender in textile printing and coating, its adhesion power much higher than the convention water-based adhesives ,different viscosities suites different applications also PVC ratios achieve different characteristics for the applied adhesive.

Coatings based on flexible PVC are non-oxidizing and permanently flexible, and are characterized by the absence of color, odor, and taste; they are not attacked at normal, vinyl chloride contributes film strength and toughness, as well as water and chemical resistance. [5]

Table 5 Studying the best ratios of clear PVC/DHP composite as flock, foil and metallic adhesives

Ratio	2	3	4	5	6
PVC%	20	30	40	50	60
DEHP %	80	70	60	50	40
Flock powder	falls	falls	falls	good	Very good
Flock sheets	falls	falls	falls	good	Very good
foil	falls	good	good	excellent	-
metallic	good	Very good	-	-	-

Table 5 shows that: ratio 3 was the successful recipe for metallic powder as aluminum or bronze powder and metallic flaks as polyester glitter ,this recipe has low viscosity so it has large ability to fill with metallic powder or flakes ,ratio3 must be free of thickening agent(Nano-silicon resin)when applied as adhesive ,the powder or flakes mixed with the clear past of PVC/DEHP in a percentage between 10% to 15% .

Ratio 5 was the suitable recipe as foil adhesive, when apply ratio 5 clear PVC/DEHP composite as foil adhesive, the printed film must be dried before foil application, foil was applied onto the printed area using heat transfer machine at 170C^{o} for 5seconds, all oil -based inks can take-off foil in random and non-suitable way but foil adhesive catch foil in homogenous and uniform film.

In case of multi-color printing with foil at same design, anti-foil must be applied in all colors except the foil adhesive ,foil has many colors and different thickness, 16 micron is the best thickness for screen printing ,cold peal technique is the suitable way for foil.

Ratio 6 shows a very good adhesive for flock sheets or powder, in case of flock sheets, the adhesive shows the best quality when thick film was printed onto the fabric and cured, the flock was applied onto the printed area using heat transfer machine, for high durability poly amide powder adhesive was recommended either by mixing with the ink or by brushing onto the printed area the suitable fixing temperature and time was 190C^{o} and 3seconds.

In case of flock powder, thick film of adhesive was printed and the flock was applied onto the printed area with electro static flocking machine, without drying the film (wet application), for much durability hardener was recommended (nylon additive), the suitable fixing temperature and time were 170C^{o} and 2 minutes using hot air convert-belt dryer, flock has many different colors and different fiber types; the famous fiber is polyester, viscose and nylon.

Table 5 shows that: adhesion power increased as the PVC percentage increased, ratio 3 preferred for metallic powder and metallic flaks due to its low viscosity and application technique (mixing) with the ink, ratio 5 suitable for foil as it is much soft than ratio 6, foil is very thin film 16mm while ratio 6 suitable for flock although its shows hard film as flock is thick film with fiber height about 0.5ml to about 1ml, so hard film not observed.

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