

Bleeding study of Nano-form (PVC/DEHP-TiO₂) Composite as Coating Substance and Printing Inks on 100% Dark Polyester Fabric

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Abstract: Bleeding is a dye migration from the dyed poly ester fabric into the printed or coated film, to avoid this problem different additive were studied as ESO, metal-metal stabilizer “CaZn “and Nano form calcium carbonate ,in this study ESO react with the liable chlorine of PVC and minimize the liberation of HCl in presence of CaZn as heat stabilizer, calcium carbonate has high efficiency as heat stabilizer and showing good filling properties reducing the ink cost, Nano-form titanium dioxide used in different ratios to achieve suitable whiteness. Suitable recipe PVC/DEHP composite which achieves high bleed resist printing and coating film reported in this study, the maximum whiteness achieved was 78.2.whiteness and particle size of all recipes were measured.

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1. Introduction

Nanoscience and nano-technology has a growing application in textile filed either in printing or finishing, most of process aimed to make up the fabric quality and productivity by improving various properties of textiles as water repellent, fire resist, anti-microbial , UV protection printing inks and coating materials which increase softness ,flexibility and appearance.

Bleeding is a dye migration from the dyed synthetic fabric into the coating and printing film casing a negative effect on the color or whiteness , it is considered as one of printing and coating disadvantage as the disperse dyestuff sublimate under high temperature during drying and fixation which lead to change the color of the film according to the background of dyed synthetic fabric ,white printing film changes into pale yellow if the background fabric was yellow ,or changes into rose if the background of the synthetic fabric was red and so on.

In this study various factors were studied to achieve the minimum bleeding and improvement the printing and coating oil-based film also minimize the evaporation of such gases as HCL gas that also keeping the inks, coating substances and processes itself environmental safety.

All inks and coating substances include additive were in Nano-form to improve quality and productivity by minimize the particle size of raw material which lead too much increasing of the surface area of printing and coating film and minimize the holes in between particles reducing the amount of dye sublimation.

Such additives make the inks and coating film more stable as it contains catalysts which reduce the drying and fixation temperature to minimum condition lead to reduce the sublimation process which is directly proportional to temperature.

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- ESORefined 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- Citrate oil ATBC is a non-toxic industrial chemical plasticizer. It shows the best performance in PVC and considered better than DEHP

Supplied by fang co ltd. China www.weiku.com

1-5- CaCO_3 supplied by El-Eyman co. Egypt

1-6- Calcium zinc supplied by Triveni chemicals, India www.trivenichemical.com/stabilizer-1.html

1-7- 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

1-100% knit red polyester fabric 130gm/m²

2-100% knit red cotton fabric 150gm/m²

Red cotton sample (blank sample) were scoured; half bleached and dyed with reactive vinyl sulfonyl dyestuff at 60C°, washed and dried

Polyester 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

4- Measuring instruments

4-1- viscometer:

Measuring according to ASTM –D562 and GB9269-88 Standard Practices for Basic Calibration of Master Viscometers and Viscosity Oil Standards



4-2-whiteness meter:

Measuring according to ASTM E313 - 10 Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates Significance and Use This practice should be used only to compare specimens of the same material and same general appearance.

4-3- 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 about 1 minute, the temperature during mixing and dispersing process must be below 60C°, 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°; 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 70Durometer 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°for 1minute using infra-red convert belt dryer.

5-6-Measuring and testing

All finished fabrics were subjected to a suitable instrument for measuring and testing according to standard international test method for each test; all instruments were calibrated before testing.

5-7-preparing and testing laboratory

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

www.spi-eg.com

6-Practical procedures

Bleed study of (PVC/DEHP/TiO₂) composite

1-Studying the best ratio of titanium dioxide and PVC/DEHP when applied on 100% dark polyester fabric

Composites with different recipes (A, B, C and D) from (PVC/DEHP/TiO₂) as reported in table 1 were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 1 and figure 1, the blank sample was applied with the same recipe onto 100% red cotton fabric.

2-Effect of ESO on bleed resists of (PVC/DEHP/30%TiO₂) composite

3%, 6%, 9%and 12% of ESO was added to composites with different recipes (E, F, I and J) from (PVC/DEHP/30%TiO₂) as reported in table 2 were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 2 and figure 2, not: The equivalent amount of added ESO was reduced from the percentage of DEHP.

3- Effect of CaZn on bleed resists of (PVC/DEHP/30%TiO₂) composite

0%, 2%, 3%and 4% of CaZn were added to composites with different recipes (K, L, M and N) of (PVC/DEHP/30%TiO₂) as reported in table 18 pastes were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 3 and figure 3.

4- Effect of CaCO₃ on bleed resists of (PVC/DEHP/30%TiO₂) composite

0%, 10%, 15%and 25% of calcium carbonate were added to composites with different recipes (O, P, Q and R) from (PVC/DEHP/30%TiO₂) as reported in table 19 were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 4 and figure 4.

5-Confirmation test for bleed resists of (PVC/DEHP/TiO₂) composite

Ratio of 25% calcium carbonate, 2%ESO and 3% CaZn, 21% titanium dioxide 24.5% PVC and 24.5DEHP were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 5 .

6-Confirmation test for bleed resists of (PVC/citrate/TiO₂) composite

Ratio of 25% calcium carbonate, 2%ESO and 3% CaZn, 21% titanium dioxide 24.5% PVC and 24.5 citrate were mixed, dispersed, milled and applied upon 100% red polyester fabrics with methodology as mention, the whiteness of all printed or coated samples were measured and reported in table 6 .

3. Results and discussion

Bleeding is the migration of disperse dye from dark polyester dyed fabric into the printed film casing color change ,bleeding considered one of the main disadvantages of printing on dyed synthetic fibers ,to overcome these problem such factors were studied as TiO₂,ESO,CaCO₃and CaZn .

Before PVC can be made into finished products, it always requires conversion into a compound by the incorporation of additives such as heat stabilizers, UV stabilizers, lubricants, plasticizers, processing aids, impact modifiers, thermal modifiers, fillers, flame retardants, blowing agents and smoke suppressors, and, optionally pigments. The choice of additives used for the PVC finished product is controlled by the cost performance requirements of the end use specification. ⁽¹⁾

1- Studying the best ratio of titanium dioxide and PVC/DEHP when applied on 100% dark polyester fabric

Table1 and figure 1 showing that: the best titanium dioxide percentage was ratio B which achieve a high whiteness value (53.7) on dark polyester fabric (red background), this is low whiteness value compared with the same recipe which achieve (83.7) on 100%cotton fabric that typically due to the dye migration from the fabric into the white printed film .

Table 1 Studying the best ratio of titanium dioxide and PVC/DEHP when applied on 100% dark polyester fabric

Ratio	A	B	C	D
PVC	50	50	40	50
DEHP	50	50	60	50
TiO ₂ %	35	30	35	40
Whiteness	38.7	53.7	44.7	53.1



Figure 1 Studying the best ratio of titanium dioxide and PVC/DEHP when applied on 100% dark poly ester fabric

2-Effect of ESO on bleed resists of (PVC/DEHP/30%TiO₂) composite

To improve the process ability and prevent the thermal degradation of poly (vinyl chloride) (PVC), various plasticizers and heat stabilizers have to be compounded. Phthalic plasticizers and metal soap stabilizers are usually used with epoxides as costabilizers.

Epoxidized soybean oil (ESO), is one of the most commonly used epoxides because of its typical combined roles as a plasticizer and heat stabilizer in PVC compounds. ESO, however, sometimes causes surface contamination of PVC compounds because saturated fatty acids such as stearic and palmitic acids in soybean oil easily bleed onto the surface. In addition, some ingredients in ESO with hydroxide groups and unreacted double bonds during epoxidization also tend to increase the bleeding of ESO. This is due to their low compatibility with PVC resins. ⁽²⁾

Epoxidized compounds are recognized as HCl scavengers, however, in the catalytic presence of ZnCl₂, they react with the chloride to produce a chemical species that is able to remove allylic chlorine atoms in PVC chains. Furthermore, it has been reported that epoxidized soybean oil (ESO) has improved the thermal stability and gamma radiation resistance of plasticized PVC compounds. ⁽³⁻⁷⁾

Table 2 Effect of adding ESO on bleed resist of 100% dark polyester fabric.

Ratio	K	L	M	N
PVC%	35	34	33.5	33
DEHP %	35	34	33.5	33
TiO ₂ %	30	30	30	30
CaZn%	0	1	2	3
Whiteness	50.6	55.2	58.4	60.4

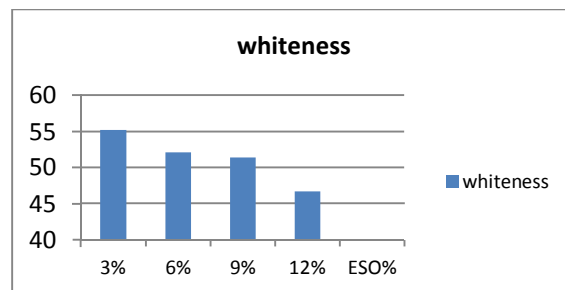


Figure 2 Effect of adding ESO on bleed resist of 100% dark polyester fabric.

The whiteness was slightly increased with addition of 3% ESO as it was shifted from 53.7 (table 1 ratio B) without adding ESO to 55.2 with addition of 3% ESO (table 2 ratio E) that means ESO improve the bleed resist of TiO₂-PVC/DEHP composite when applied on 100% polyester fabric.

Table 2 and figure 2 showing a clear decrease in whiteness with the increase of ESO% from 3% to 12%, meaning that: the ESO % was inversely proportional to the whiteness, negative result obtained with 12%.

Such advantages were observed when ESO was added to the composites at low concentration as it has an excellent effect on film sharpness specially when printing on cloth mesh as it keep the holes of the fabric open, also has improve the thermal stability and increase the softness of printing and coated film.

3- Effect of CaZn on bleed resists of (PVC/DEHP/30%TiO₂) composite

Degradation is a chemical change that reduces the average molecular weight of the polymer, since the mechanical integrity of plastics invariably depends on their high average molecular-weight, any significant extent of degradation typically weakens the material, weathering degradation of plastics results in their surfaces impart micro cracking, yielding micro particles that continue on in the environment, known as 'micro plastics.' Micro-plastics concentrate Persistent Organic Pollutants (POPs). ⁽⁸⁾

Thermal stability was improved by the presence of DEHP and ESO. In addition, improved color stability was achieved with intermediate CaSt₂/ZnSt₂ and CaZn ratios, and minimal HCl release was achieved in formulations, results can be directly applied to design a formulation for a specific application. ⁽⁹⁾

The low thermal stability of polyvinyl chloride (PVC) has limited the use of this polymer in industry. There have been many attempts to improve the

thermal stability and mechanical properties of this polymer in recent years.

As polyvinyl chloride decomposes and loses HCl even at lower processing temperature, it is assumed that the active hydrogen is apparently replaced in PVC. It is possible to inhibit the eliminated HCl by organometallic salts.

Since the level of epoxidization improves the glass transition temperature (T_g), and the second phase order transition of PVC is a thermodynamic process we have studied the thermal effect of different levels of epoxidization of ESBO-PVC. In this paper we wish to report the stability of PVC with calcium, barium and zinc stabilizers.⁽¹⁰⁻¹³⁾

One of the most crucial additives is heat stabilizers, these agents minimize loss of HCl, a degradation process that starts above 70 °C. Once dehydrochlorination starts, it is autocatalytic, many diverse agents have been used including, traditionally, derivatives of heavy metals (lead, cadmium). Increasingly, metallic soaps (metal "salts" of fatty acids) are favored, species such as calcium stearate or calcium zinc.⁽¹⁴⁾

Table 3 Effect of CaZn on bleed resist (PVC/DEHP/30%TiO₂) composite when applied on 100 red polyester fabrics

Ratio /gm.	O	P	Q	R
PVC	35	35	35	35
DEHP	35	35	35	35
TiO ₂	30	30	30	30
CaCO ₃ %	0	10%	15%	25%
Whiteness	58.4	69.2	69.7	71.6

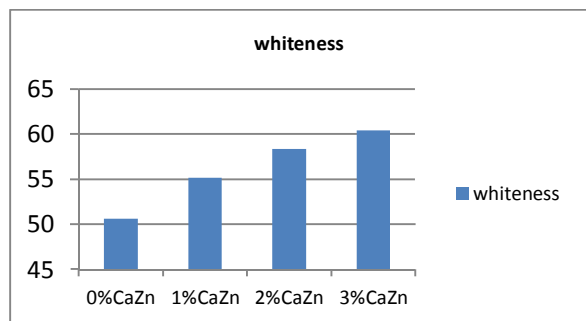


Figure 3 Effect of CaZn on bleed resist (PVC/DEHP/30%TiO₂) composite when applied on 100 red polyester fabrics

Table 3 and figure 3 showing that the CaZn has a positive effect on bleeding, it considered as thermal stabilizer the best percentage which clearly improve the bleed resist of (TiO₂-PVC/DEHP) composite was 3% which achieves 60.4 whiteness values, the whiteness value was shifted from 53.7 (table 1 ratio

B) to 60.4 as shown in (table 3 ratio N) also it is environmental friendly as it minimize the evaporated HCL under curing conditions.

4 -Effect of CaCO₃ on bleed resists of (PVC/DEHP/30%TiO₂) composite

Fillers are used to improve strength and stiffness, to lower cost, and to control gloss. The most common filler is calcium carbonate. It ranges in size from 0.07 to well over 50 mm. Some forms are treated with a stearic acid coating. Clay fillers, such as calcined clay, improve electrical properties. Glass fibers, talc, and mica improve tensile strength and stiffness.⁽¹⁵⁾

A moderate effect was observed for PVC/nano-CaCO₃ binary nano composites. The elongation at break increased with increasing the nano-CaCO₃ concentration. Transmission electron microscopy (TEM) study demonstrated that the nano-CaCO₃ particles were dispersed in a PVC matrix uniformly, and a few nanoparticles agglomeration was found. The toughening effect of the nano-CaCO₃ particles on PVC could be attributed to the cavitation of the matrix.

The evaluation of rheological properties revealed that the introduction of nano-CaCO₃ particles into PVC resulted in a remarkable increase in the melt viscosity.⁽¹⁶⁾

Table 4 Effect of CaCO₃ on bleed resist of (PVC/DEHP/30%TiO₂) composite when applied on 100% red polyester fabrics

Ratio /gm.	O	P	Q	R
PVC	35	35	35	35
DEHP	35	35	35	35
TiO ₂	30	30	30	30
CaCO ₃ %	0	10%	15%	25%
Whiteness	58.4	69.2	69.7	71.6

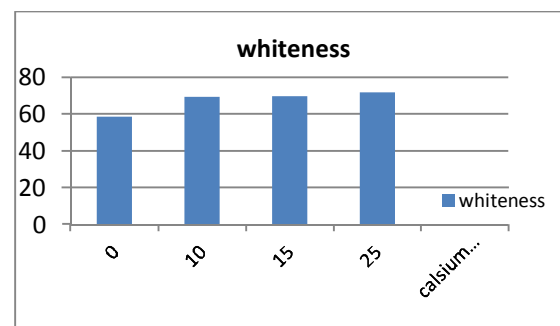


Figure 4 Effect of CaCO₃ on bleed resist of (PVC/DEHP/30%TiO₂) composite when applied on 100% red polyester fabrics

Table 4 and figure 4 showing that the bleeding is inversely proportional to the percentage of calcium carbonate, the maximum bleed resist obtained at 25% calcium carbonate with whiteness value 71.6.

5-Confirmation test for bleed resists of (PVC/DEHP/TiO₂) composite

Table 5- The best combination ratios of low bleed white applied on 100% polyester dark fabric.

Whiteness	PVC	DEHP	Titanium Dioxide	ES	CaZn	CaCO ₃
78.1	24.5 %	24.5	21 %	2%	3%	25%

From bleeding study we can come to conclusion that: ESO shows a positive effect when applied in low concentration on bleeding also it was useful in presence of metal stabilizer as CaZn In bleed resist , 2%ESO was recommended, 3 % of metal-metal stabilizer and 25% of CaCO₃ showing excellent bleed resist white film with whiteness result 78.1 .

As a result of confirmation test the percentage of main components as PVC, DEHP and titanium dioxide were reduced due to the higher percentage of calcium carbonate as shown in table 5 TiO₂%reduced from 30% to 21%, PVC percentage reduced from 35% to 24.5% and DEHP percentage was reduced from 35% to 24.5%.

The successful bleed resist recipe which achieves highest value of whiteness on 100% dark polyester fabric reflects an economy result due to the higher percentage and low price of calcium carbonate which considered as bleed resist and filling agent.

6-Bleed study of (PVC/ Citrate /TiO₂) composite

Table 6- The best combination ratios of low bleed white applied on 100% polyester dark fabric.(PVC/ Citrate /TiO₂)

Whiteness	PVC	DEHP	Titanium Dioxide	ES	CaZn	CaCO ₃
81.2	24.5 %	24.5	21 %	2%	3%	25%

From bleed study of citrate/PVC composites table 33 showing that the maximum value of whiteness was obtained with the recipe reported in illustrated table as PVC/DEHP bleed resist composite which reported in table 5, the whiteness value was

increased with citrate/PVC composites than that of DEHP/PVC composite , the maximum value was 81.2

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