Formaldehyde – Unavoidable or Avoidable Risk in Pigment Printing

Dr. Karl Siemensmeyer, Fr. Dr. Oihana Elizalde, Fr. Dr. Maria-Theresa Hechavarria-Fonseca, Karl-Heinz Weigert, Stefan Kuhn, Rolf Strobel*,

BASF SE
67056 Ludwigshafen
Germany

*BTC – Speciality Chemical Distribution GmbH
50825 Köln
Germany

Summary

Formaldehyde releasing compounds are widely used as crosslinkers in the textile industry. However, recently the standards set by legislators, as well as brands and retailers are getting stricter. BASF has now developed a formaldehyde-free Helizarin® pigment printing system that not only meets these standards, but also fulfills the quality requirements – identical to the state of the art technology.

Formaldehyde as a potential carcinogen has been the subject of debate since the 1980s. Since April 2004, formaldehyde has been classified as a Class 3 carcinogen by the IARC (International Agency for Research on Cancer).

France has gone a step further in this regard by enforcing a requirement that from January 2007 formaldehyde in all production processes be treated as a Class 1 carcinogen, though at present classification as a Class 3 carcinogen remains in place throughout the EU.

From a technical point of view, however, formaldehyde-based and formaldehyde-releasing components have so far been the most effective, cost-efficient, widely used crosslinkers in the textile industry. Comprehensive replacement of these chemicals is generally not possible. In any case, replacement is always associated with slightly increased costs for the textile industry.

Crosslinkers are widely used in the textile industry for such applications as resin finishing, pigment printing, pigment dyeing and coating. In addition to formaldehyde-based crosslinking systems, crosslinkers based on isocyanate and blocked isocyanate are commonly used. But the problem with these is their high reactivity and short shelf life (isocyanates), or problematic blocking groups (blocked isocyanates, butanonoxime). New crosslinking systems need to be developed if the goal of formaldehyde-free pigment printing is to be achieved.

Sources of formaldehyde in pigment printing

Crosslinkers are not the only source of formaldehyde in textile printing paste. It is generally also present in acrylate dispersions employed as binders and sometimes in the synthetic thickeners.

Formaldehyde in acrylate dispersions is due to:

a) the N-methylolacrylamide or N-methylolmethacrylamide crosslinker monomers in the polymer dispersions
b) the initiator system for radical polymerization

These two sources contribute about 50 % each to the formaldehyde content on a printed fabric, as comparative tests with appropriate binder dispersions show (cf. Table 1).

Table 1: Formaldehyde values of different binder dispersions

Binder	Type	Formaldehyde content on the fabric according to Law 112
Binder 1	Standard binder for pigment printing	47 ppm
Binder 2	Binder 1, produced with formaldehyde-free initiator system	23 ppm
Binder 3	Binder 2, without crosslinker	4 ppm
Substrate used(cotton)		4 ppm

Liquid, synthetic thickeners are dispersions based on crosslinked polyacrylic acids. These are often polymerized by the same initiator system as acrylate dispersions. They therefore also have a definite formaldehyde content and contribute to the formaldehyde level on the fabric.

In addition to these basic components, numerous other auxiliaries are used to modify, for example, the printability, running properties, fastness properties and handle. Often these are multifunctional auxiliaries that may also contain crosslinkers.

The effective formaldehyde content of the pigment print therefore depends strongly on the recipe. But in every case, the biggest contributor, as all measurements show, is the crosslinker, followed by the binder dispersion.

Therefore, to produce formaldehyde-free pigment prints, it is necessary to select or manufacture not only a suitable binder and crosslinker, but also a thickener and other auxiliaries.

The formaldehyde-free Helizarin® pigment printing system

Helizarin® Fixing Agent TX 4737 is a new crosslinker polymer from BASF with reactive centers that is free of formaldehyde, isocyanate and blocked isocyanate.

At the same time, a new formaldehyde-free acrylate binder for textiles, Helizarin® Binder TX 4738, was specially developed to be compatible with the new crosslinker polymer. The reactive centers of Helizarin® Binder TX 4738 are designed to react with Helizarin® Fixing Agent TX 4737 under the standard fixation conditions of pigment printing to form a wash-resistant network.

Formaldehyde-free synthetic thickeners are available on the market, such as Lutexal® GP ECO as a powder thickener and Lutexal® TX 4606 as liquid thickener. These formaldehyde-free thickeners fit perfectly with the new formaldehyde-free Helizarin® pigment printing system.

In addition, the following auxiliaries are suitable for formaldehyde-free pigment printing: Luprintol® PE New and Luprintol® MP as emulsifiers, and Luprimol® SIG, Luprintol® SE, Luprintol® TX 4732 and Luprintol® VSN as softeners.

Application properties

Tests on the formaldehyde levels of the new pigment printing system are summarized in Table 2. The tests were performed by a modified determination method analogous to LAW 112 to lower the detection limit.

Table 2: Formaldehyde content of ready-to-print, pretreated cotton and formaldehyde-free pigment prints and dyeings

Recipe components (amounts in g/kg)		Cotton	Blank pigment print paste	Pigment dyeing
	Helizarin® Binder TX 4738		100	40
	Helizarin® Fixing Agent TX 4737		3	3
	Lutexal® TX 4733		40	
	Siligen® FA			10
	Diammonium phosphate			4
	Helizarin® Blue BT			3
	Defoamer TC ECO New		1	1
	Ammonia		1	1
	Luprintol® PE New		5	5
	Water		Add to 1000	Add to1000
Formaldehyde level on the fabric (values in ppm)		**4**	**4**	**3**

With this method, the cotton used for the tests showed a value of 4 ppm formaldehyde. After applying a typical formaldehyde-free pigment dyeing recipe, a value of 3 ppm was found.

Printing with a blank print paste yielded 4 ppm. The conclusion is obvious. The chemistry used and application of the new crosslinking and binder system in combination with the thickener did not change the blank value. The chemistry used, therefore, does not contribute at all to the formaldehyde value of the pigment-printed or pigment-dyed fabric.

Table 3: Printing recipes for fastness comparison (all amounts in g/kg)

Recipe components	Recipe 1	Recipe 2	Recipe 3	Recipe 4
Helizarin® Binder ET 95	100	100		
Helizarin® Fixing Agent LF		8		
Helizarin® Binder TX 4738			100	100
Helizarin® Fixing Agent TX 4737			5	15
Defoamer TC ECO New	1	1	1	1
Luprintol® PE New	5	5	5	5
Helizarin® Blue BT	20	20	20	20
Lutexal® TX 4733	40	40	40	40
Drying	3 min at 100 °C			
Fixation	5 min at 150 °C			

Comparative tests on the standard of fastness of the new binder system were carried out in the laboratory. The recipes and process temperatures used are given in Table 3.

Recipe 1 is crosslinker-free and Recipe 2 contains a typical crosslinker for pigment printing with a low formaldehyde value. Both are simple standard recipes with a conventional binder system.

Recipe 3 is a typical recipe for a formaldehyde-free print paste with the new formaldehyde-free binder system for medium depths of shade on cotton. Recipe 4 is a comparable recipe for polyester-cotton blended fabrics – here in the ratio 65/35. The prints and the results of the Helizarin® brush-wash-at-the-boil test are shown in Table 4 (printing on cotton) and Table 5 (printing on a polyester/cotton blend).

Table 4: Fastness comparison between formaldehyde-free and conventional Helizarin® pigment printing systems on cotton

	Recipe 1	Recipe 2	Recipe 3
Print Helizarin® brush wash at the boil			

The upper portion of the print shows the original print on cotton, while the lower portion shows the result of Helizarin® brush washing at the boil. This is a BASF test method giving a good result for these simple conditions without substantial optimization.

Table 5: Fastness comparison between formaldehyde-free and conventional Helizarin® pigment printing systems on polyester/cotton 65/35

	Recipe 1	Recipe 2	Recipe 4
Print Helizarin® brush wash at the boil			

A comparable result is obtained on polyester/cotton, but with a tendency for the standard of fastness for all print pastes to be somewhat lower (cf. Table 5).

Initial trial with formaldehyde-free Helizarin® pigment printing system

Figure 1: Detail of printed design during first trial run

Table 6: Stock paste for first trial run

Water	850
Ammonia 25 %	3
Luprintol® PE New	7
Defoamer TC ECO New	2
Helizarin® Binder TX 4738	100
Helizarin® Fixing Agent TX 4737	8
Luprimol® SIG	10
Lutexal® HVW	1
Lutexal® GP ECO	12

In an initial trial run, two colors (green shades) of the six-color design shown in Fig. 1 were printed using the formaldehyde-free Helizarin® pigment printing system. The stock paste recipe is given in Table 6. The pigment concentrations were 12.2 g/kg and 2.5 g/kg.

The print pastes were prepared by the customer's usual process following the order of the recipe. Preparing the pastes did not cause any problems such as separation, agglomeration or coagulate formation. During the print run,
3600 m of fabric was printed at a speed of 40 m/min. The run took approx. 90 minutes and there were no problems such as blocking of the screens with either galvano or standard

125-mesh screens. Subsequent screen washing-off took place without problem and without the need to wash off by hand. The resulting print had an identical standard of fastness to the standard system.

Another bulk trial was carried out to perform the fastness comparison in more detail. The aim was to compare the standard of fastness of the formaldehyde-free Helizarin® pigment printing system and the customer's standard system under conditions that were kept as constant as possible. At the same time, the standard of fastness was to be adjusted to that obtained by the customer with the standard pigment printing system.

Second trial with formaldehyde-free Helizarin® pigment printing system

To compare the standard of fastness of the formaldehyde-free Helizarin® pigment printing system, the customer's recipe was converted to a formaldehyde-free Helizarin® pigment printing recipe (cf. Table 7).

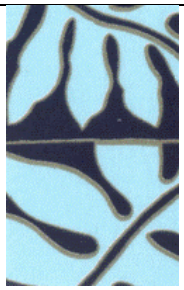
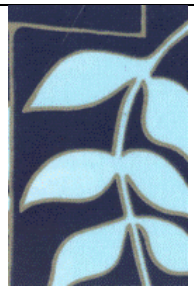
It was important to replace all components that could contribute to the formaldehyde level of the fabric.

Table 7: Printing recipes for fastness comparison (all amounts in g/kg)

Formaldehyde-free		Standard	
Water	759	Water	760
Defoamer TC ECO New	5	Antifoam	5
Luprintol® MP	12	Emulsifier	18
Luprimol® SE	7	Softener	12
Luprimol® TX 4732	10	Fixing Agent	10
Helizarin® Fixing Agent TX 4737	10	Thickener	30
Lutexal® TX 4733	37	Binder	160
Helizarin® Binder TX 4738	160		

Prints on woven and knitted fabrics were compared. A printing speed of 30 m/min was used throughout. The fabric was subsequently dried at 110 °C and fixed with hot air for 5 minutes at 150 °C.

Table 8: Comparison of prints and fastness properties

	Formaldehyde-free Helizarin® pigment printing system		Standard printing system	
	Knitted fabric	Woven fabric	Knitted fabric	Woven fabric
Original print				
	Household wash 60 °C			
5 x household wash 60 °C (evaluated according to DIN EN ISO 105 A02)	 4 – 5	 4	 4	 4
Rub fastness, dry (DIN EN ISO 105-X12)	4 – 5	4 – 5	4 - 5	4 – 5
Rub fastness, wet (DIN EN ISO 105-X12)	3 – 4	3	3	3
Fastness to dry cleaning (DIN EN ISO 105-D01)	4	4	4	4

In all cases the printing results were excellent (cf. Table 8). Moreover, in each case, the standard of wash fastness to household washing, here 5 x 60 °C, was identical (cf. Table 8).

Within the usual experimental error for such tests, comparison of the dry and wet rub fastness properties determined according to DIN EN ISO 105-X12, showed a similar standard of fastness. If anything, the formaldehyde-free Helizarin® pigment printing system tended to give somewhat better results than the standard printing system (cf. Table 8).
In addition, tests on the fastness to dry cleaning according to DIN EN ISO 105-D01 showed that the new formaldehyde-free pigment printing system has a fastness level comparable to that of the current standard (cf. Table 8)

Table 9: Comparison of measured formaldehyde values (ppm)

	Knitted fabric	Woven fabric
Formaldehyde-free Helizarin® pigment printing system	4	4
Standard pigment printing system	89	96
Unprinted cotton	4	4

The low (4 ppm) formaldehyde level of prints produced with the new Helizarin® pigment printing system on both woven and knitted fabrics shows that in every case a formaldehyde level corresponding to the lowest possible value, that of the original cotton, was reliably obtained. In contrast to this, the standard printing system used as a comparison yielded formaldehyde levels that were more than 20 times higher (89 ppm on knitted fabric and 96 ppm on woven fabric, cf. Table 9).

Summary

The formaldehyde-free Helizarin® pigment printing system meets the requirements of the industry with regard to running properties and standard of fastness. A very good standard of fastness, at least identical to the state of the art, is achieved and ensured.

The use of Helizarin® Binder TX 4738 and Helizarin® Fixing Agent TX 4737 guarantees absolutely formaldehyde-free chemistry. In combination with other components of the formaldehyde-free Helizarin® pigment printing system –

Thickeners: Lutexal® GP ECO
Lutexal® TX 4606
Lutexal® TX 4733

Emulsifiers: Luprintol® PE New

	Luprintol® MP
Softeners:	Luprimol® SIG
	Luprimol® SE
	Luprimol® TX 4732
	Luprimol® VSN

– it is ensured that no formaldehyde is added and the lowest possible formaldehyde level on the fabric is consistently obtained during pigment printing. No additional measures to reduce the formaldehyde level are required to obtain Oekotex Standard class 1.